Collisional Breakup in a Quantum System of Three Charged Particles

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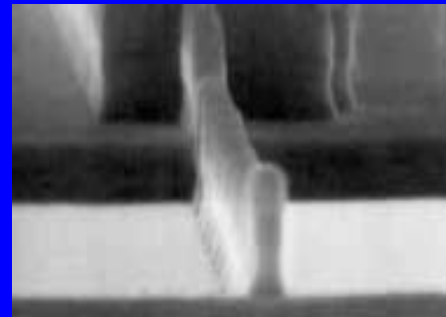
- **Collaborators: Tom Rescigno (LBNL), Dan Horner (U.C. Berkeley), Mark Baertschy (University of Colorado) and William Isaacs (LLNL)**
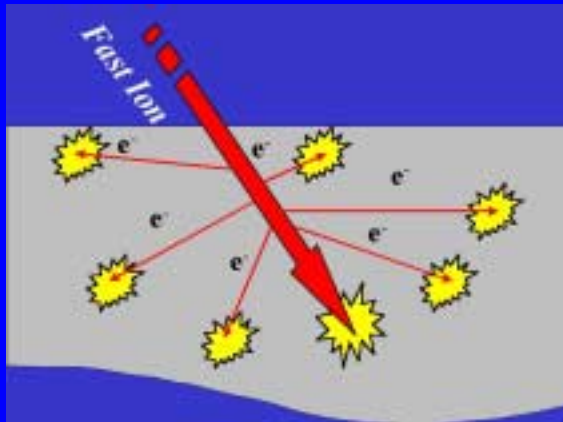
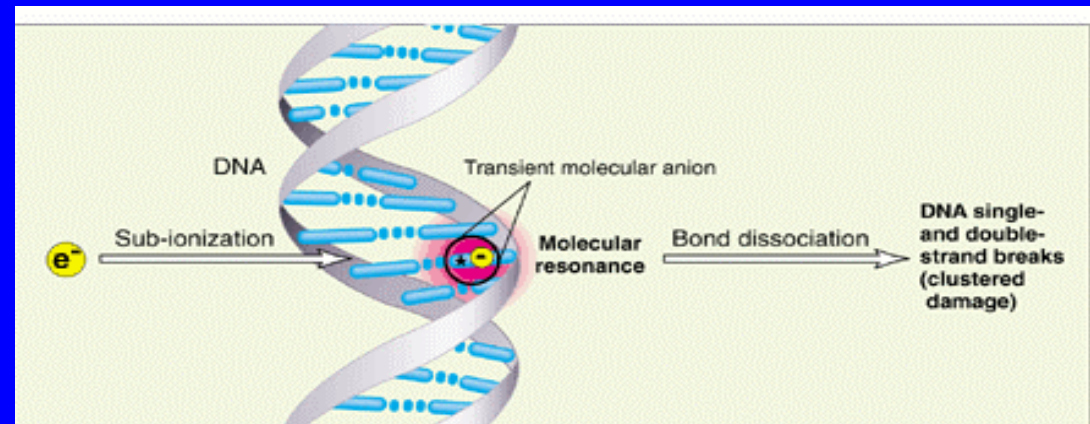# Electronic Collisions Drive a Multitude of Common Physical Devices and Chemical Changes

High Intensity Plasma Arc Lamp (OSRAM-Sylvania)

Plasma-etched Gate 0.12 microns wide, (Bell Labs --Lucent Technologies)

Cascades of secondary electrons from ionizing radiation

Electronic dissociative attachment causes most breaks in DNA strands from radiation

Electron Impact Processes

$\bullet e^- + M \rightarrow e^- + M^*$ **Electronic excitation (Any symmetry *and* singlet to singlet *and* singlet to triplet)**

$\bullet e^- + M \rightarrow e^- + A + B$ **Electron impact dissociation**

$\bullet e^- + M \rightarrow A^- + B$ **Dissociative attachment**

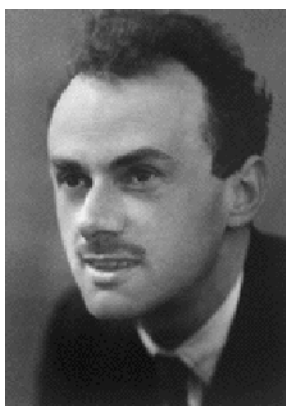$\bullet e^- + M \rightarrow e^- + e^- + M^+$ **Electron impact ionization**

Contrast photoexcitation and photoionization

$\bullet h\upsilon + M \rightarrow M^*$

$\bullet h\upsilon + M \rightarrow M^+ + e^-$

**Dipole Selection rules!
NO singlet to triplet excitation**

Collisions and Electronic Structure of Atoms and Molecules

Schrodinger Equation: $\quad H\Psi = E\Psi \qquad i\hbar\,\dfrac{\partial\Psi}{\partial t} = H\Psi$

P. A. M. Dirac: "*The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.*"

In the year 2002 we are still solving them:

- Walter Kohn and John Pople won Nobel Prize in 1998 for Density Functional Theory (DFT) and the application of computational chemistry. *DFT addresses lowest energy state only.*

- Theoretical Chemistry and Molecular Physics are still full of hard problems -- excited states, dynamics, reactions, condensed phases...

Quantum Mechanics of Two-Electron Systems

A (very) brief history:

- Hylleraas (1930's) and Pekeris (1950's) -- developed the formalism and the algorithms to compute the "exact" bound states of helium.

- 1961-- C. Schwartz solved the scattering problem for e⁻+ H elastic collisions

- 1961 to 1990 -- excitation cross sections below ionization threshold, first computed accurately by P. Burke and coworkers.

- 1993 -- I. Bray and A. Stelbovics computed excitation above IP and *total* ionization cross section.

The formal theory of ionization was worked out in the 1960's by Rudge and Seaton and by Peterkop, but has never been implemented numerically to solve the scattering problem.

Why is this two-electron problem so hard?

- Electron impact ionization (of hydrogen) was the only two-electron problem not completely "solved" by the 1990s.

- All other aspects of two-electron problems except those with two electrons in the continuum were solved by then, in the sense of being *completely reduced to practical computation*.

Collisions and Electronic Structure of Atoms and Molecules

All interactions between the particles involved are Coulombic: $V \sim q_1 q_2/distance$. So the nonrelativistic theory is perfectly well posed.

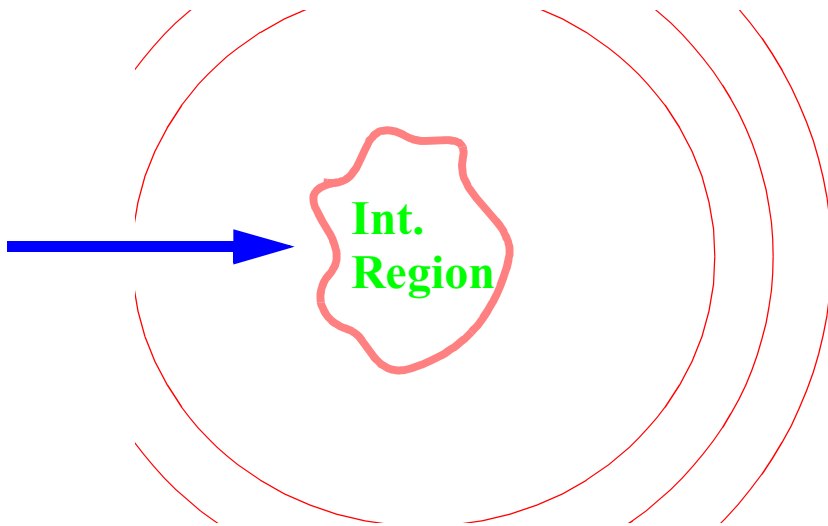*The difference between bound states and collisions: boundary conditions in the Schrödinger equation $H\Psi = E\Psi$*

- **Bound states:** as $r \to \infty$ the wave function vanishes $\Psi \to 0$, **the energy E is the unknown of an eigenvalue problem.**

- **Scattering states:** e. g. $\Psi \to e^{i\boldsymbol{k} \bullet \boldsymbol{r}} + f(\vartheta, \varphi)\dfrac{e^{ikr}}{r}$ (for one particle) and the energy is **known.**

The Scattering Amplitude, $f(\vartheta, \varphi)$, is the unknown

The Collision Problem

Map "incoming" to "outgoing" free solns

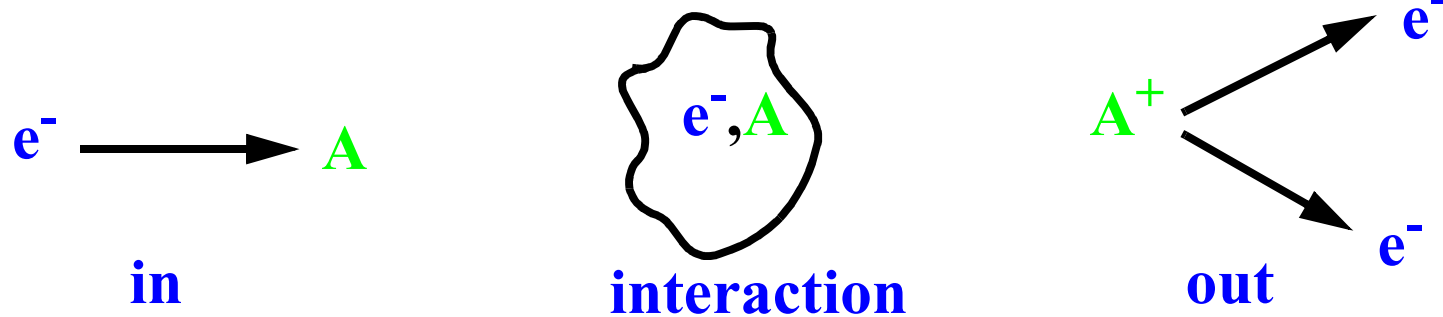$$\Psi_{in} \rightarrow \Psi_{interaction} \rightarrow \Psi_{out}$$

Solve $H\Psi = E\Psi$

with boundary conditions (one particle):

$$\Psi \rightarrow e^{i\boldsymbol{k} \bullet \boldsymbol{r}} + f(\vartheta, \varphi)\frac{e^{ikr}}{r}$$

in   out

The e - 2e Problem

e⁻ $\longrightarrow$ A   e⁻,A   A⁺ → e⁻ / e⁻

in   interaction   out

Long-range Potentials: "Coulomb potentials are forever"

- Like gravitational attraction the, potential goes like $V \sim -\dfrac{1}{r}$ and force like $F \sim -\dfrac{1}{r^2}$
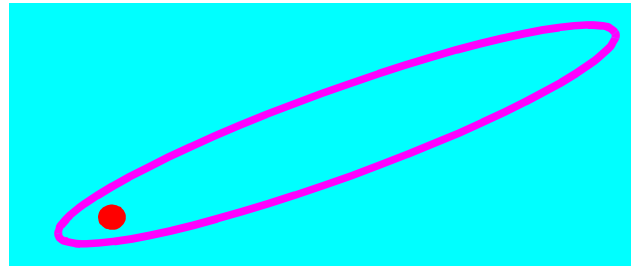
- In classical mechanics: Kepler orbits, "infinitely long" eliptical orbits (e.g. comets), a vector constant of the motion along their major axis (Runge-Lenz vector).

$$\Psi \rightarrow e^{i(\boldsymbol{k} \bullet \boldsymbol{r} + \eta \ln(kr - \boldsymbol{k} \bullet \boldsymbol{r}))} + f(\vartheta, \varphi)\frac{e^{i(kr - \eta \ln 2kr)}}{r}$$

- In quantum mechanics: logarithmic phases for electron scattering from an ion and for photoionization

But Coulomb potentials are even more special when two particles are unbound

Qualitative aspects of the physics of the (e,2e) process

• "Recoil" and "Binary" peaks in the Triple Differential Cross Section
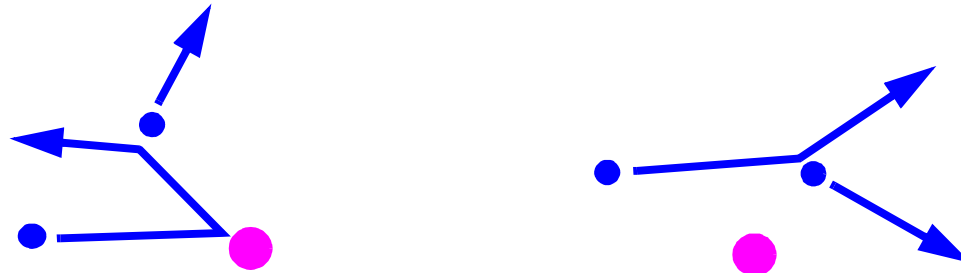
• The Wannier threshold law $\sigma \propto E^{1.127}$

• "Wannier geometry" for ejection near threshold: Four decades of semiclassical investigation of the threshold physics.

• "Smile" in the Single Differential Cross Section at higher energies: more probable final states have one electron fast, the other slow.

The Formal Theory of Coulomb Three-Body Breakup

The asymptotic form of the wave function for ionization was first given by Peterkop (1962) and Rudge and Seaton (1965):

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \sim -f(\hat{r}_1, \hat{r}_2, \alpha) i^{1/2} \left(\frac{K^3}{\rho^5}\right)^{1/2} e^{i\left(K\rho + \dfrac{\zeta(\hat{r}_1, \hat{r}_2, \alpha)}{K} ln(2K\rho)\right)}$$

where $\rho = \left(r_1^2 + r_2^2\right)^{1/2}$ **and** $\tan\alpha = r_2/r_1$ **are the hyperradius and associated angle,**

$K = (2E)^{1/2}$, $\zeta(\hat{r}_1, \hat{r}_2, \alpha) = (\sin\alpha)^{-1} + (\cos\alpha)^{-1} - (1 - \cos\vartheta_{12}\sin 2\alpha)^{-1/2}$ **and**

$f(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2, \alpha)$ **is the associated amplitude.**

- *Matching to this form has proved to be computationally impractical to date because the logarithmic phase depends on all angles in the problem -- and it is not separable in spherical coordinates.*

Also, The Formal Theory Requires a Special Mechanism to Extract the Cross Section From the Exact Wave Function

The ionization amplitude is given by an expression involving *effective charges* because the standard formula, $f = \langle \Phi_{final} | V_{interaction} | \Psi^{(+)} \rangle$ has an *infinite phase*

$$f(\vec{k}_1, \vec{k}_2) = -(2\pi)^{5/2} e^{i\Delta(\vec{k}_1, \vec{k}_2)} \langle \Phi^{(-)}_{\vec{k}_1, z_1} \Phi^{(-)}_{\vec{k}_2, z_2} | V_{12} | \Psi^{(+)} \rangle$$

with

$$\Delta(\vec{k}_1, \vec{k}_2) = 2[(z_1/k_1)\ln(k_1/K) + (z_2/k_2)\ln(k_2/K)]$$

and *effective charges* that satisfy a condition dependent on the momenta (and directions) of the escaping electrons

$$\frac{z_1}{k_1} + \frac{z_2}{k_2} = \frac{1}{k_1} + \frac{1}{k_2} - \frac{1}{|\vec{k}_1 - \vec{k}_2|}$$

Exterior Complex Scaling -- A Complete Theory For The Two-Electron Atomic Breakup Problem

Goals:

- Rigorously apply the boundary conditions of the formal theory of ionization to an *ab initio* solution of the time-independent Schrödinger equation -- *without using them explicitly.*

- Correctly extract the cross section for break-up from the solution of the time-independent Schrödinger equation
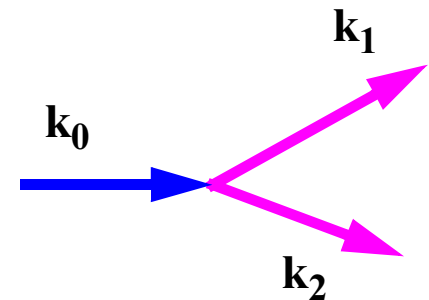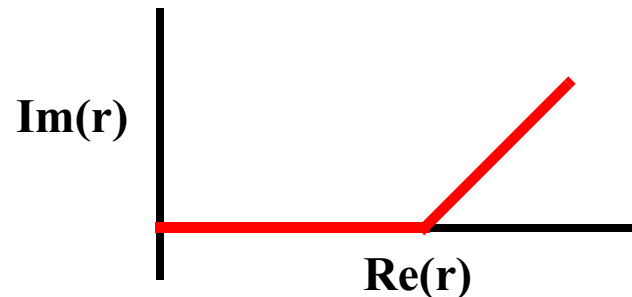
Solve for the Scattered Wave

$$|\Psi^+\rangle = |\Phi^0_{k_0}\rangle + |\Psi^+_{sc}\rangle \quad \textbf{satisfying:} \quad (H - E)|\Psi^+_{sc}\rangle = (H - E)|\Phi^0_{k_0}\rangle$$

Exterior Complex Scaling

The mapping $r \to R(r)$ **can be written as**

$$R(r) \equiv \begin{cases} r & , r < R_O \\ R_O + (r - R_O)e^{i\phi} & , r \geq R_O \end{cases}$$

The idea is to make R_0 **large enough so that the potential can be safely truncated beyond that point. The full contour is used to construct** $\Psi_{sc}^{+}(R(r))$, **but the cross sections are evaluated over the finite volume (or surface) where all coordinates are real.**

Exterior Complex Scaling Transforms Outgoing Waves into Exponentially Decaying Functions

$Re(e^{ikr})$ on the real axis
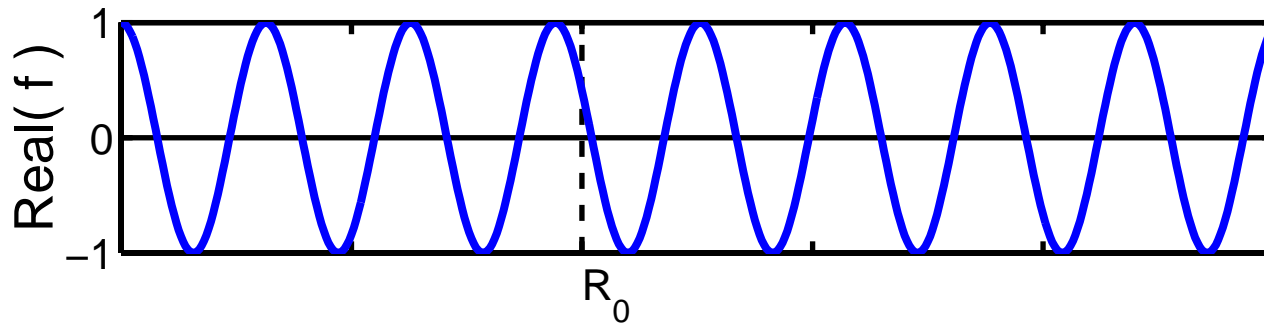
$Re(e^{ikR(r)})$ on the exterior scaling contour
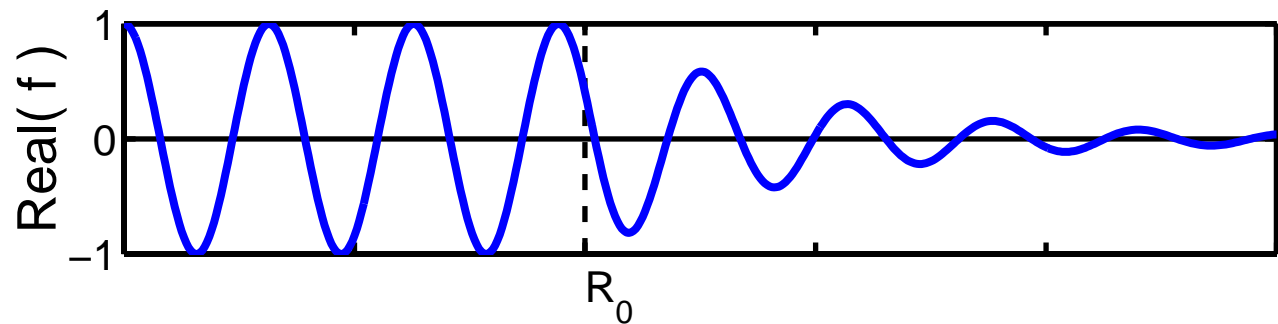
Exterior Scaling in Two Radial Dimensions

To implement exterior scaling, the grid points are laid out along the complex contour, making sure the point R_0 is one of the nodes, so that the cusp discontinuity conditions can be satisfied.
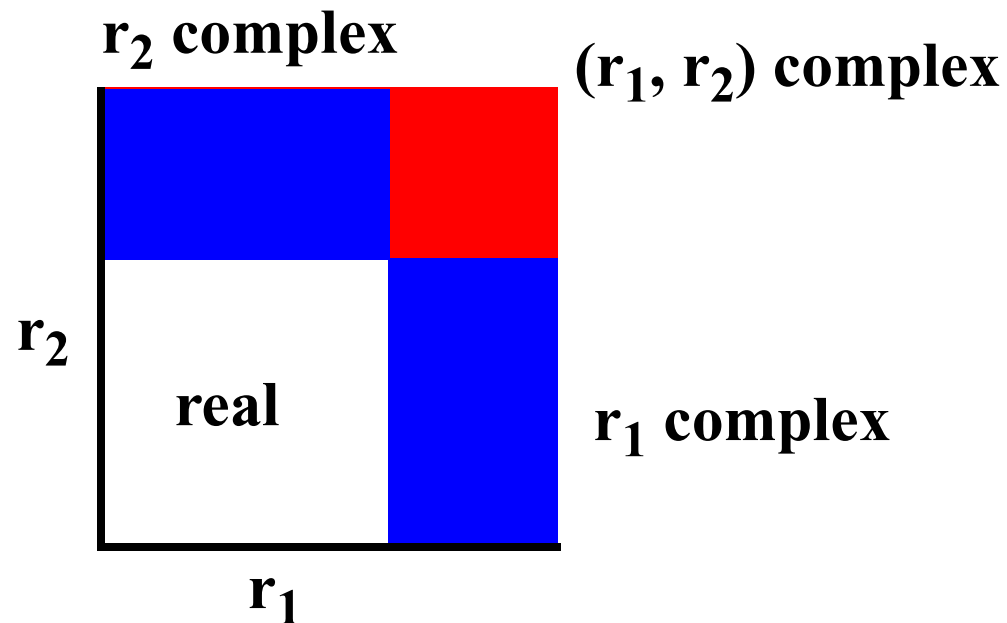
Each dimension: 458 points, R_0 = 100 a_o, R_{max} = 125 a_o, $\vartheta = 40°$

Numerical Implementation for Electron-Hydrogen Ionization

Angular momentum expansion:

$$\Psi^+_{sc}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_1 r_2} \Sigma_{L, l_1, l_2} \psi^L_{l_1, l_2}(r_1, r_2) y^{L, 0}_{l_1, l_2}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$$

Example parameters from the initial calculations treating the entire problem:

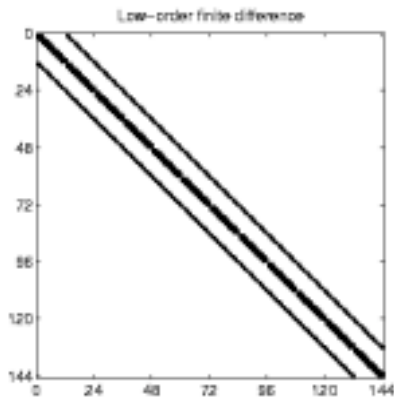458 grid points in each dimension = 209,764 total grid points
- Solution of linear equations: Use SuperLU to solve sparse system of 209,764 linear eqs. for each (l_1, l_2) block

For a typical L > 2 calculation with coupling of 24 (l_1, l_2) pairs:
- Conjugate Gradient Squared (CGS) using preconditioning from solution for uncoupled equations for each (l_1, l_2) pair, required 30-40 iterations.
- Sparse system is of dimension 24 x 209,764 = 5,034,336
- Solution required ~2.8 hours with 48 cpus of T3E for each set of eqs.

Using Recent Applied Math Developments in Numerical Linear Algebra: Direct Sparse Solvers

Precondition

Precondition

High-order finite difference

Low-order finite difference

$$\begin{array}{ccccc} A_{0,0} & d_{0,1} & d_{0,2} & d_{0,3} & \cdots \\ d_{1,0} & A_{1,1} & d_{1,2} & d_{1,3} & \cdots \\ d_{2,0} & d_{2,1} & A_{2,2} & d_{2,3} & \cdots \\ d_{3,0} & d_{3,1} & d_{3,2} & A_{3,3} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{array} \begin{array}{c} \psi^0_{0,0} \\ \psi^0_{1,1} \\ \psi^0_{2,2} \\ \psi^0_{3,3} \\ \vdots \end{array} = \begin{array}{c} \chi^0_{0,0} \\ \chi^0_{1,1} \\ \chi^0_{2,2} \\ \chi^0_{3,3} \\ \vdots \end{array}$$
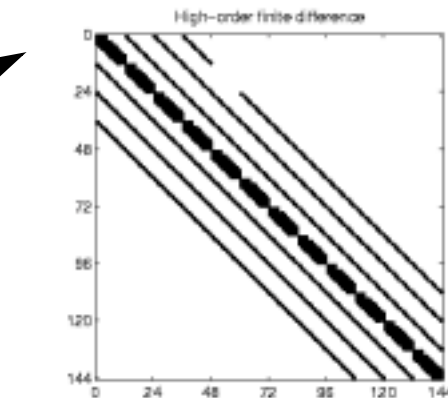
Conjugate Gradient, high-order finite difference

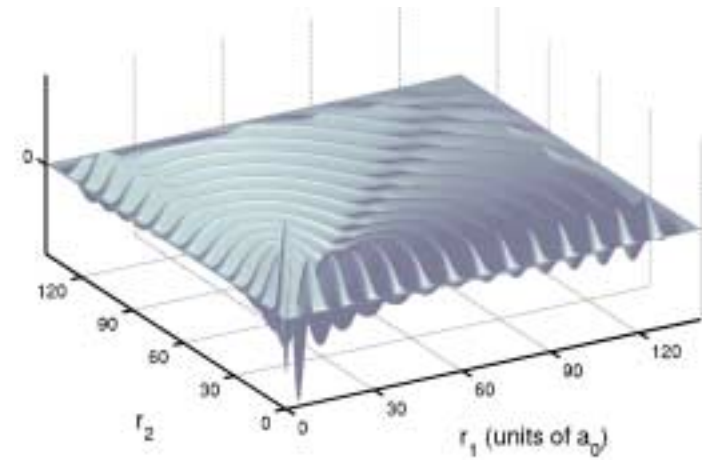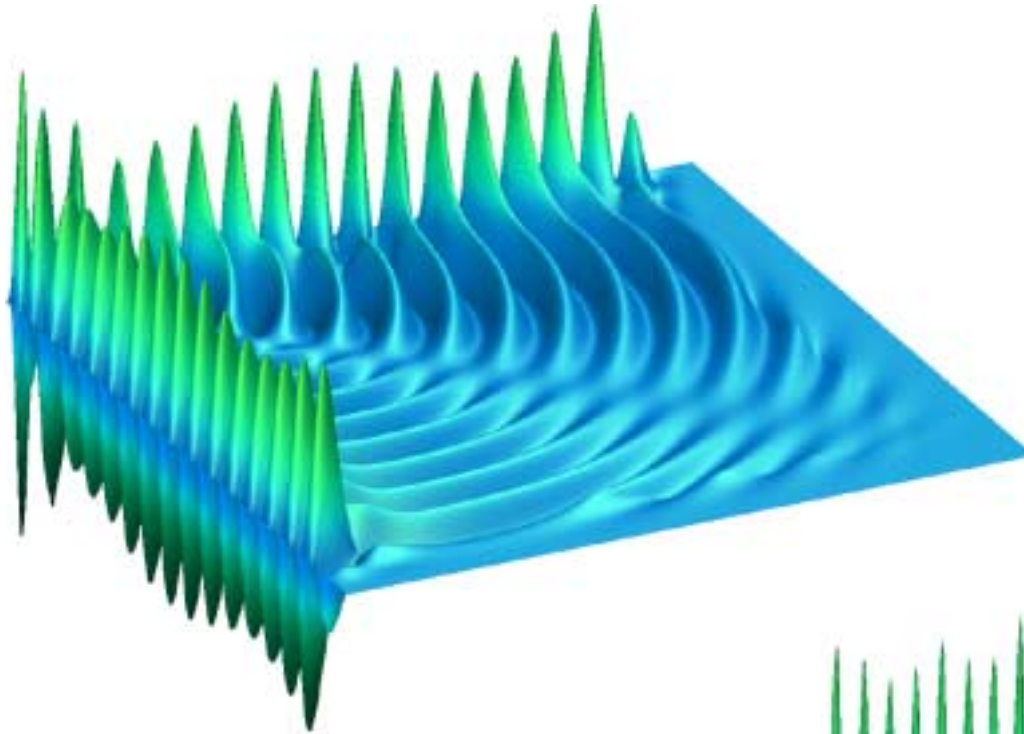**SuperLU -- direct sparse solver, low-order finite difference, uncoupled blocks**

Conjugate Gradient, full equations with coupled $l_1 l_2$ blocks

$\psi^{L}_{l_1, l_2}(r_1, r_2)$

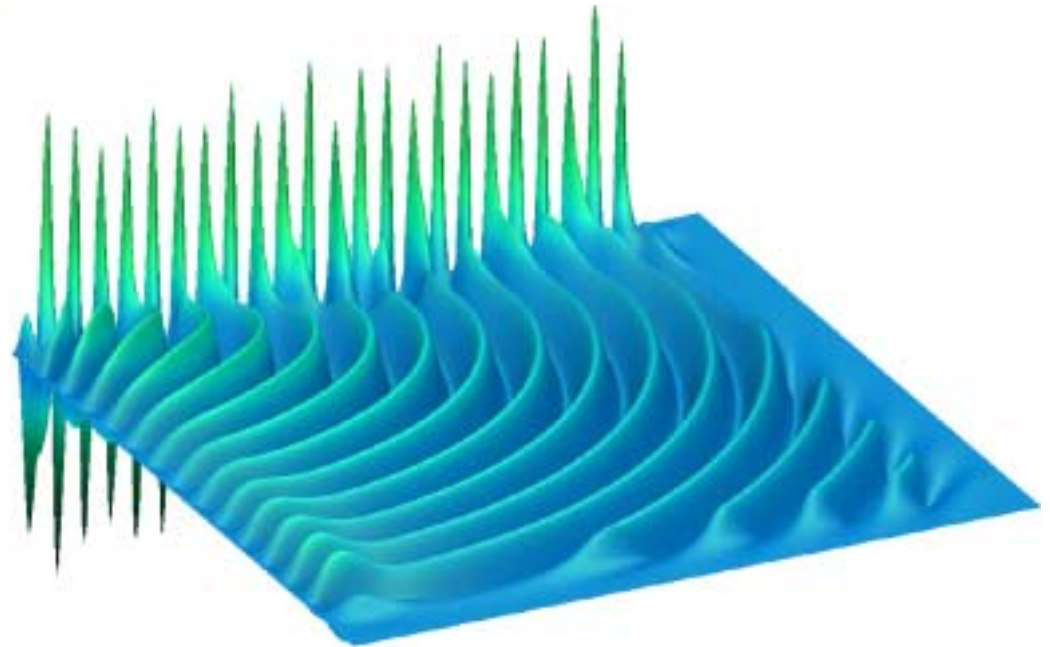Wave function, $l_1 = l_2 = 1$

r_2

r_1

r_2 r_1 (units of a_0)
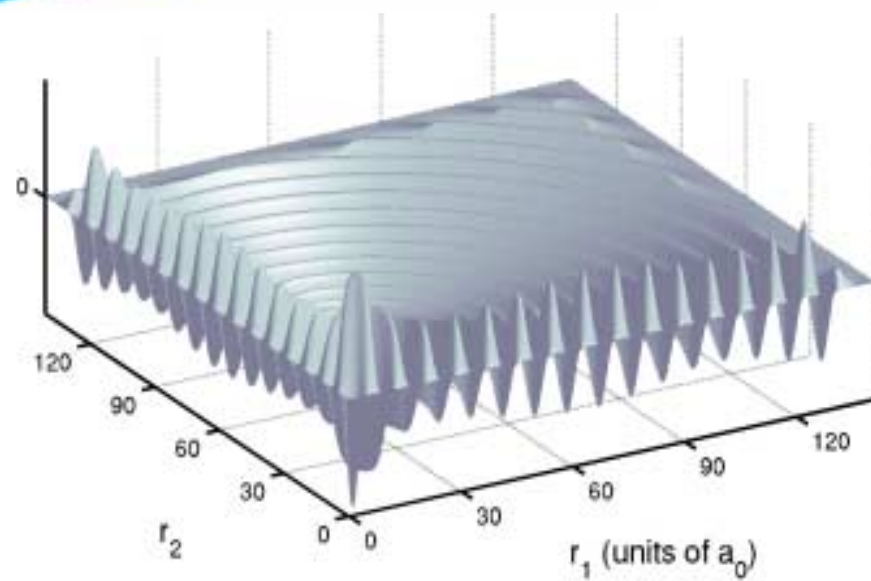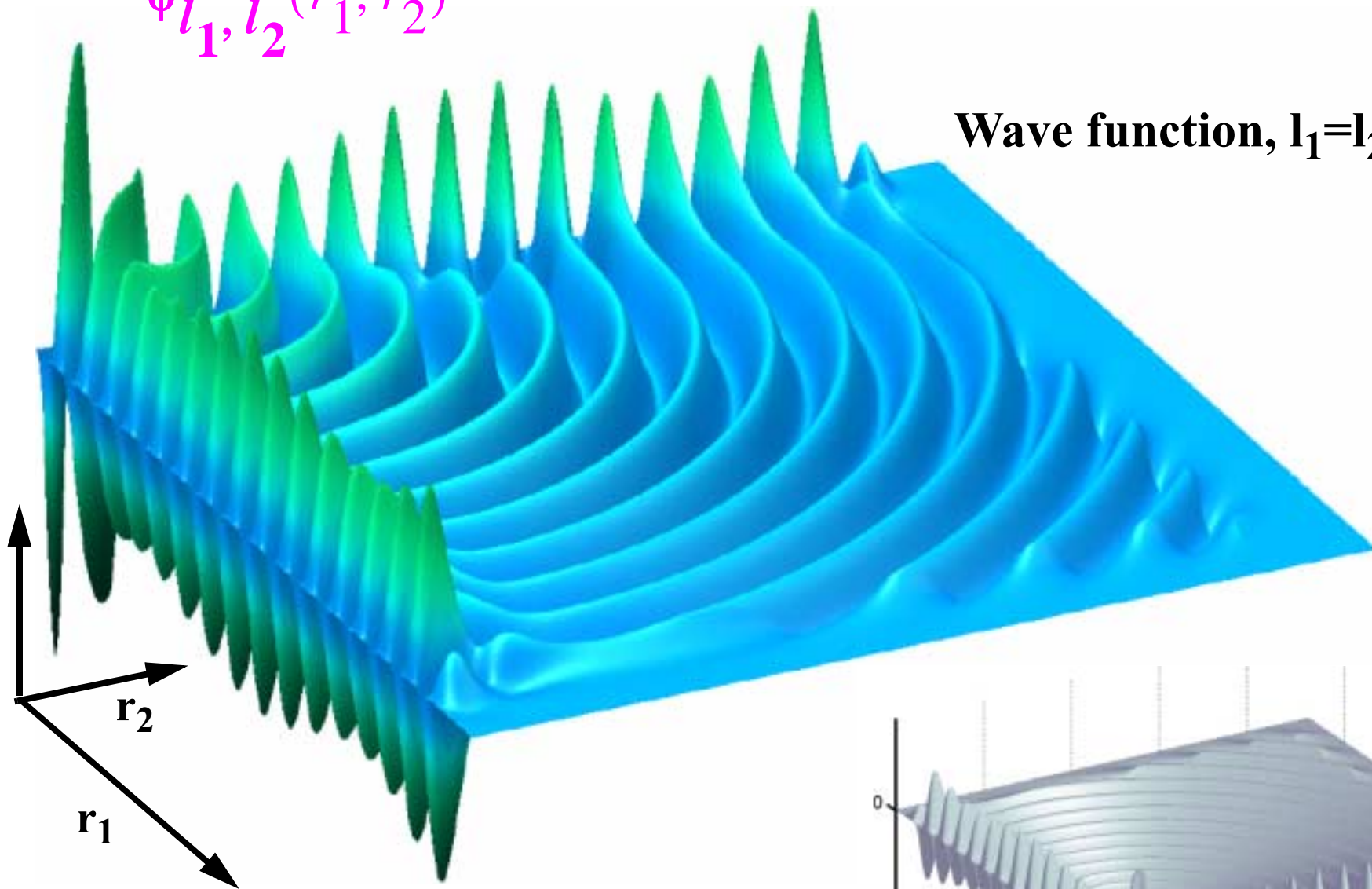
Wave function, triplet, $l_1=l_2=1$

Wave function, l_1, l_2 different

Experimental Cross Sections and Geometries

Triply Differential Cross Sections (TDCS) are differential in Energy and two angles, given for a particular energy sharing. They are a representation of the most detailed information: $\sigma(\vec{k_1}, \vec{k_2})$.

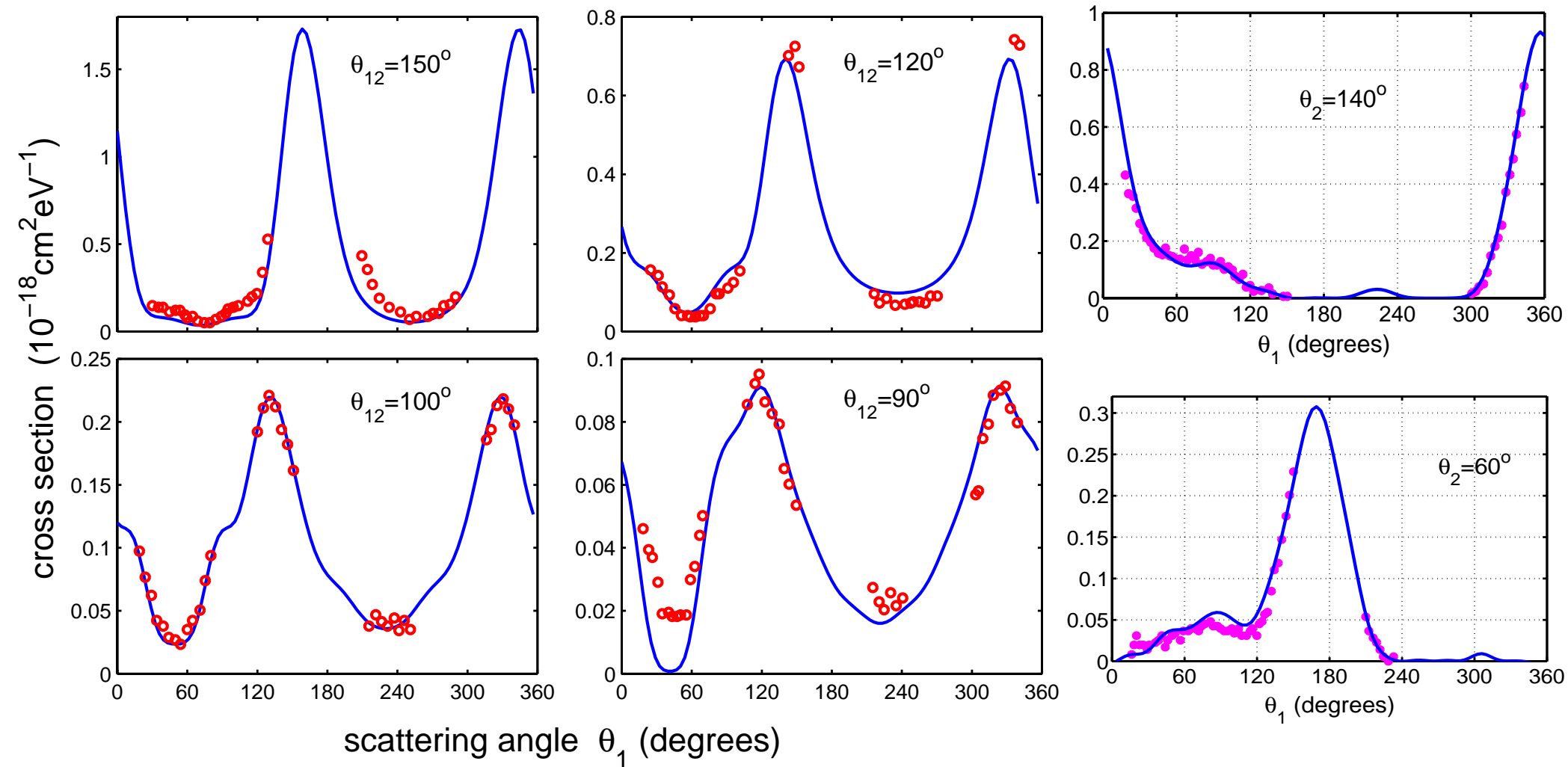**Doubly Differential Cross Section** (DDCS) is $\sigma(\vec{k_1}, k_2) = \int \sigma(\vec{k_1}, \vec{k_2}) d\hat{k}_2$

Singly Differential Cross Section (SDCS) is: $\sigma(k_1, k_2) = \int\int \sigma(\vec{k_1}, \vec{k_2}) d\hat{k}_1 d\hat{k}_2$

Coplanar Scattering Geometry: Symmetric Coplanar means $\varepsilon_1 = \varepsilon_2$
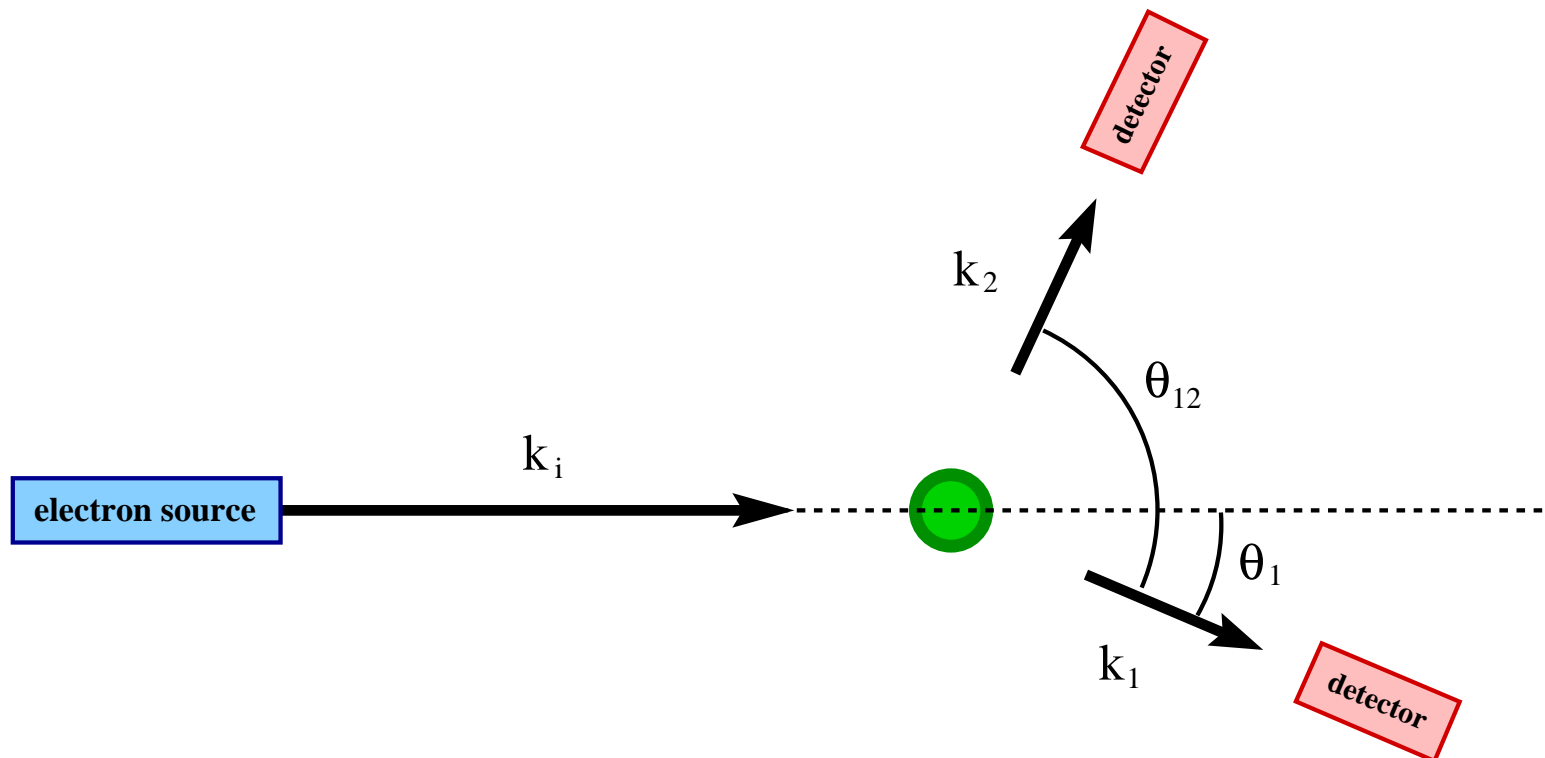
Triple Differential Cross Sections -- Symmetric Coplanar 17.6eV

Experiments of Röder et al. 1996.

The natural extension of the integral formula for breakup amplitudes for short-range potentials to the Coulomb case

"Two-potential" formula

$$f(k_1, k_2) = \langle \varphi_{k_1}^{(-)} \varphi_{k_2}^{(-)} | E - T + 1/r_1 + 1/r_2 | \psi_{sc} \rangle$$

- $Z = 1$ in final Coulomb functions necessary to eliminate one-body terms with numerical problems akin to "disconnected diagrams"
- For finite grids, the calculation of ψ_{sc} the Coulomb potentials are truncated (at the edge of the exterior scaled grid), and a finite *overall* phase does not change the observables.
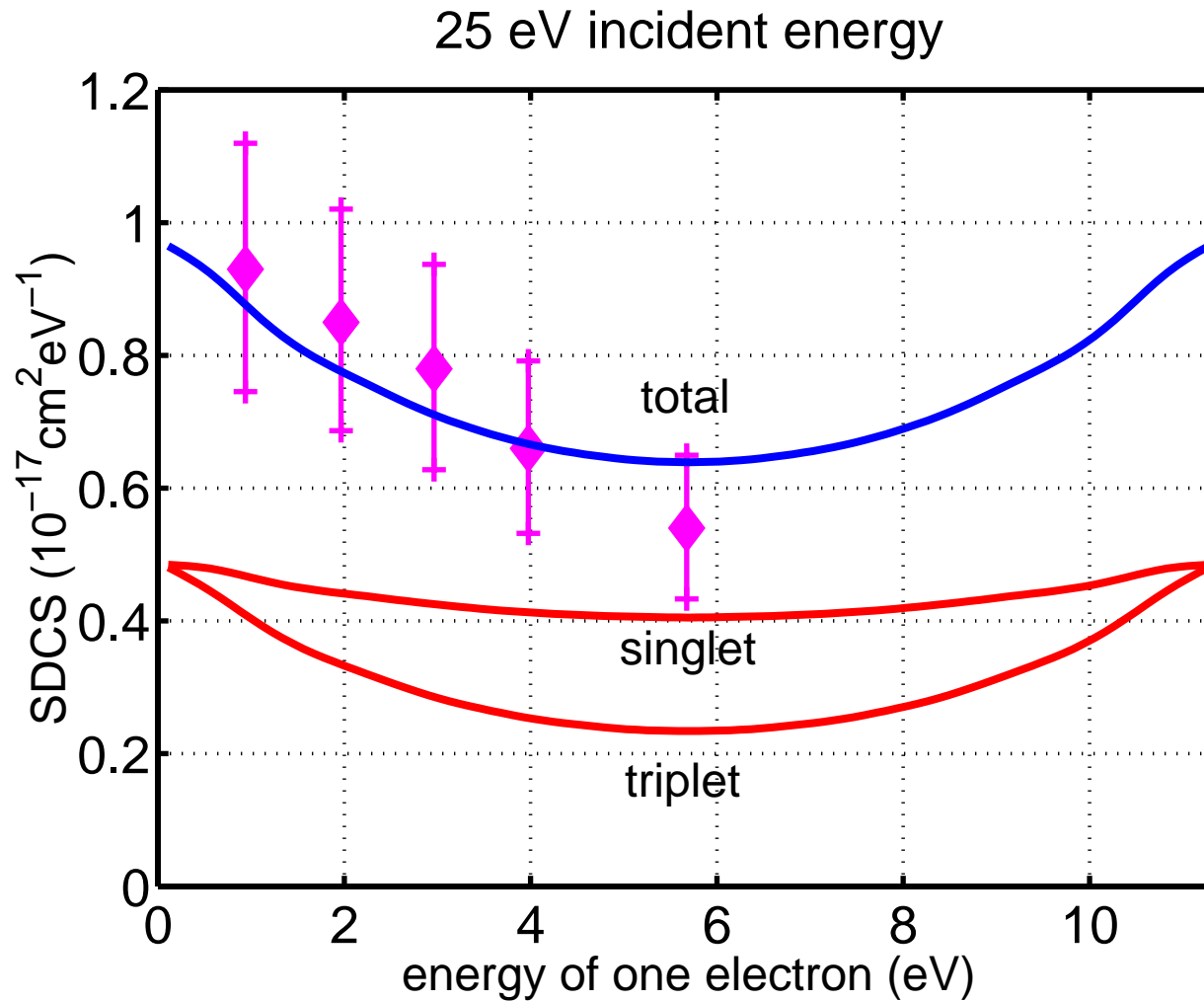
Note also, surface integral form:

$$f(k_1, k_2) = \frac{1}{2} \int_S (\varphi_{k_1}^{(-)} \varphi_{k_2}^{(-)} \nabla \psi_{sc} - \psi_{sc} \nabla \varphi_{k_1}^{(-)} \varphi_{k_2}^{(-)}) \bullet \hat{n} dS$$

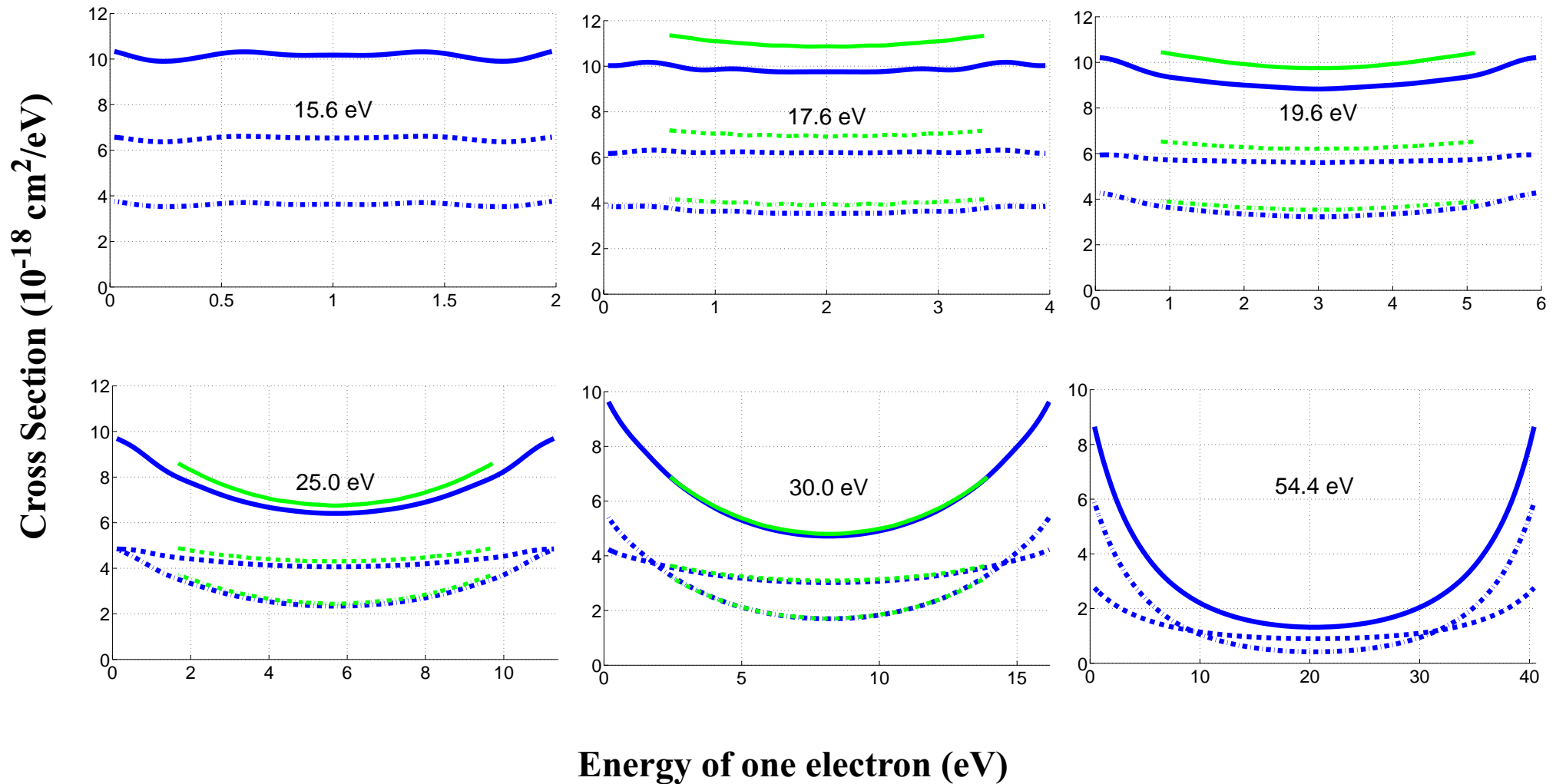**Triply Differential Cross Sections -- Symmetric Coplanar 17.6 eV
Compare integral form with flux extrapolation**
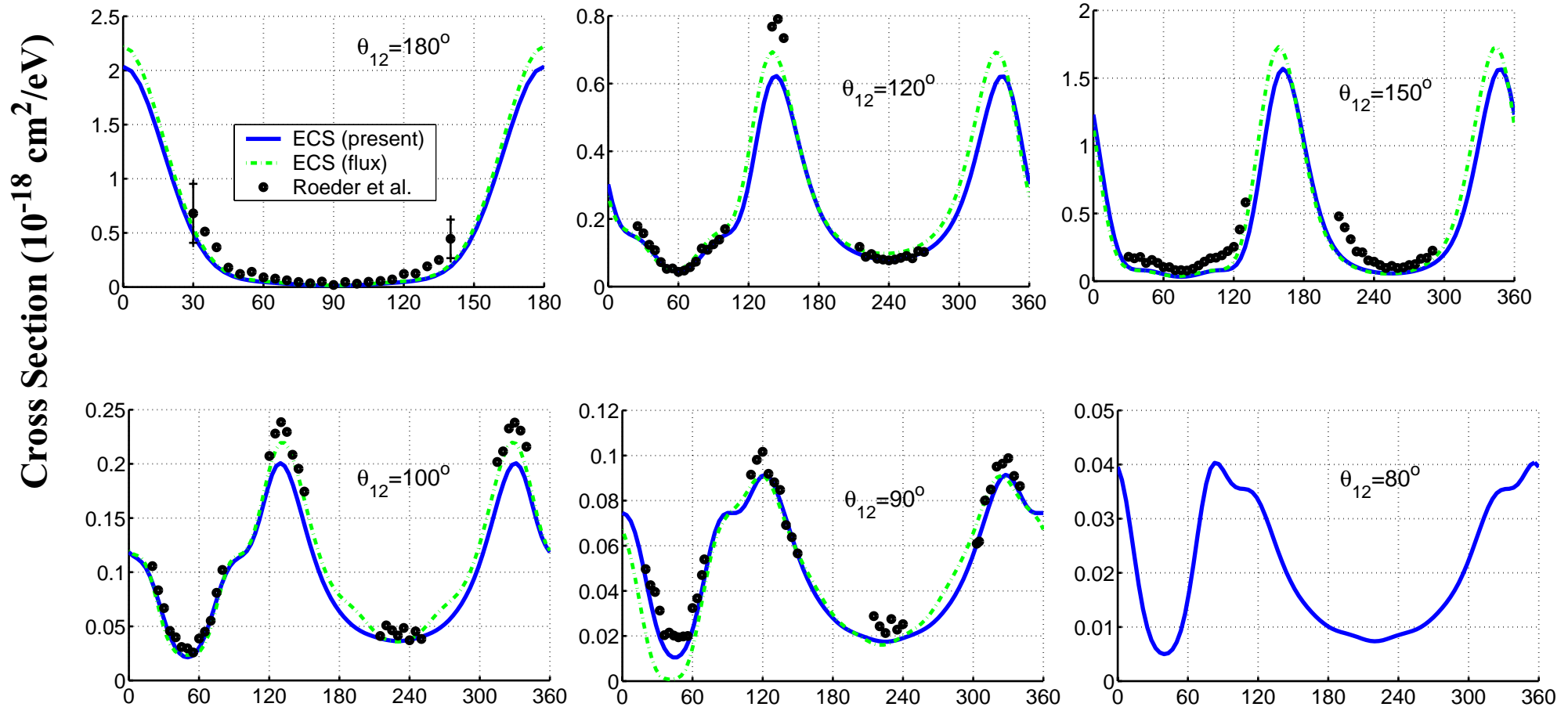
Singly Differential Cross Section at 25 eV


25 eV incident energy

Singly Differential Cross Sections, $\sigma(k_1, k_2) = \iint \sigma(\mathbf{k}_1, \mathbf{k}_2) d\hat{\mathbf{k}}_1 d\hat{\mathbf{k}}_2$,
(integral form and flux: singlet, triplet and total)

Cross Section (10^{-18} cm^2/eV) (y-axis)

15.6 eV, 17.6 eV, 19.6 eV, 25.0 eV, 30.0 eV, 54.4 eV

Energy of one electron (eV) (x-axis)

Triply Differential Cross Sections Can be Described with Great Accuracy -- Symmetric Coplanar 30eV
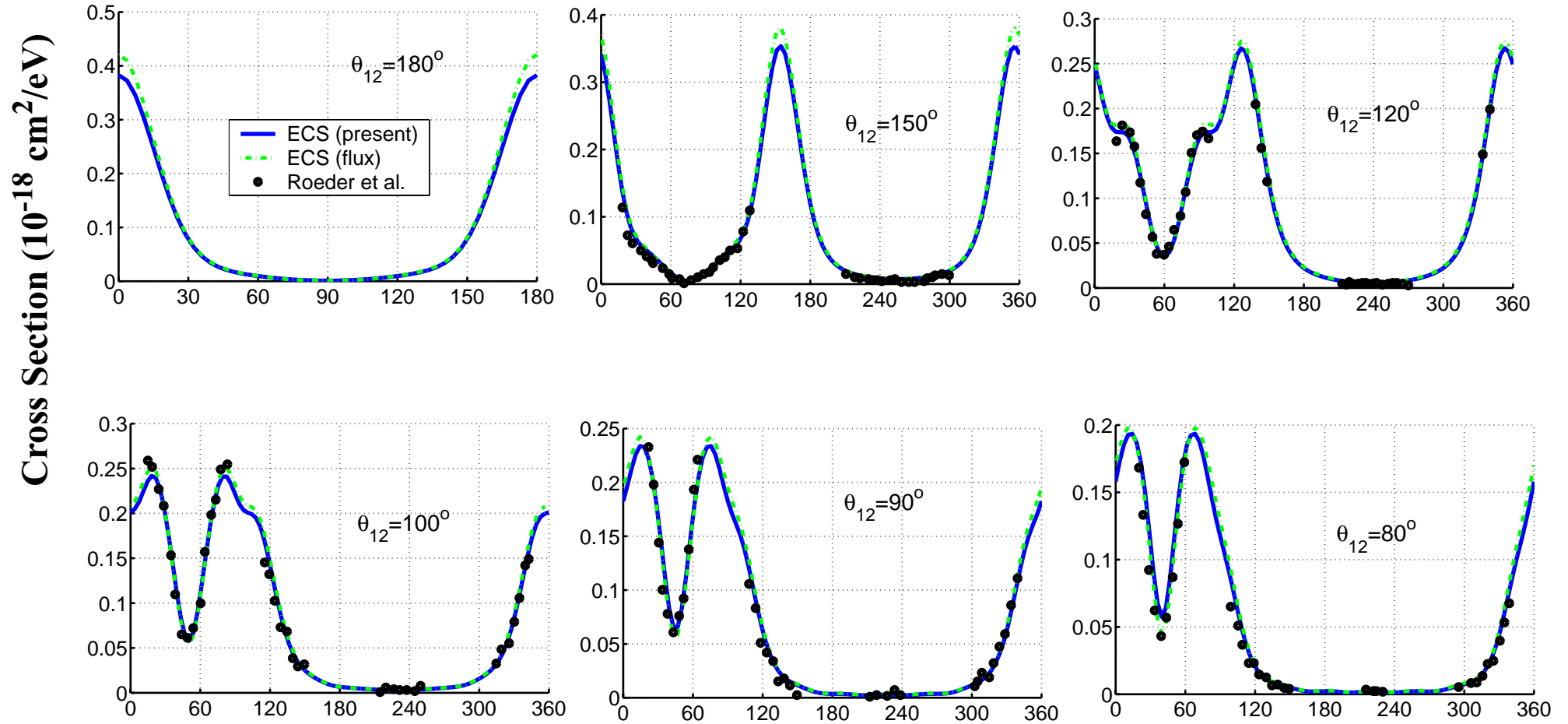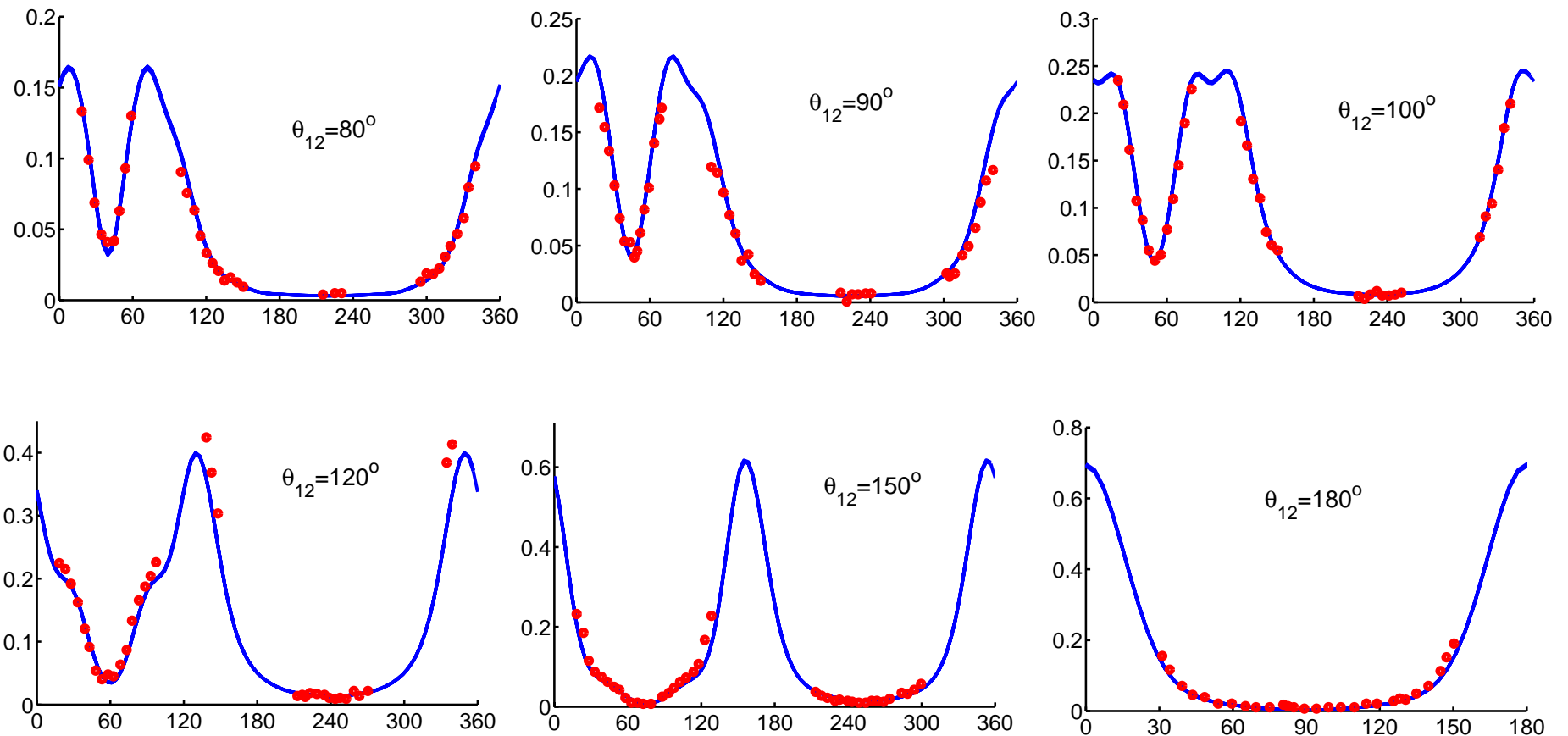
"Integral Form" Allows Calculations at Lower Energies: Triply Differential Cross Sections -- Symmetric Coplanar 15.6 eV
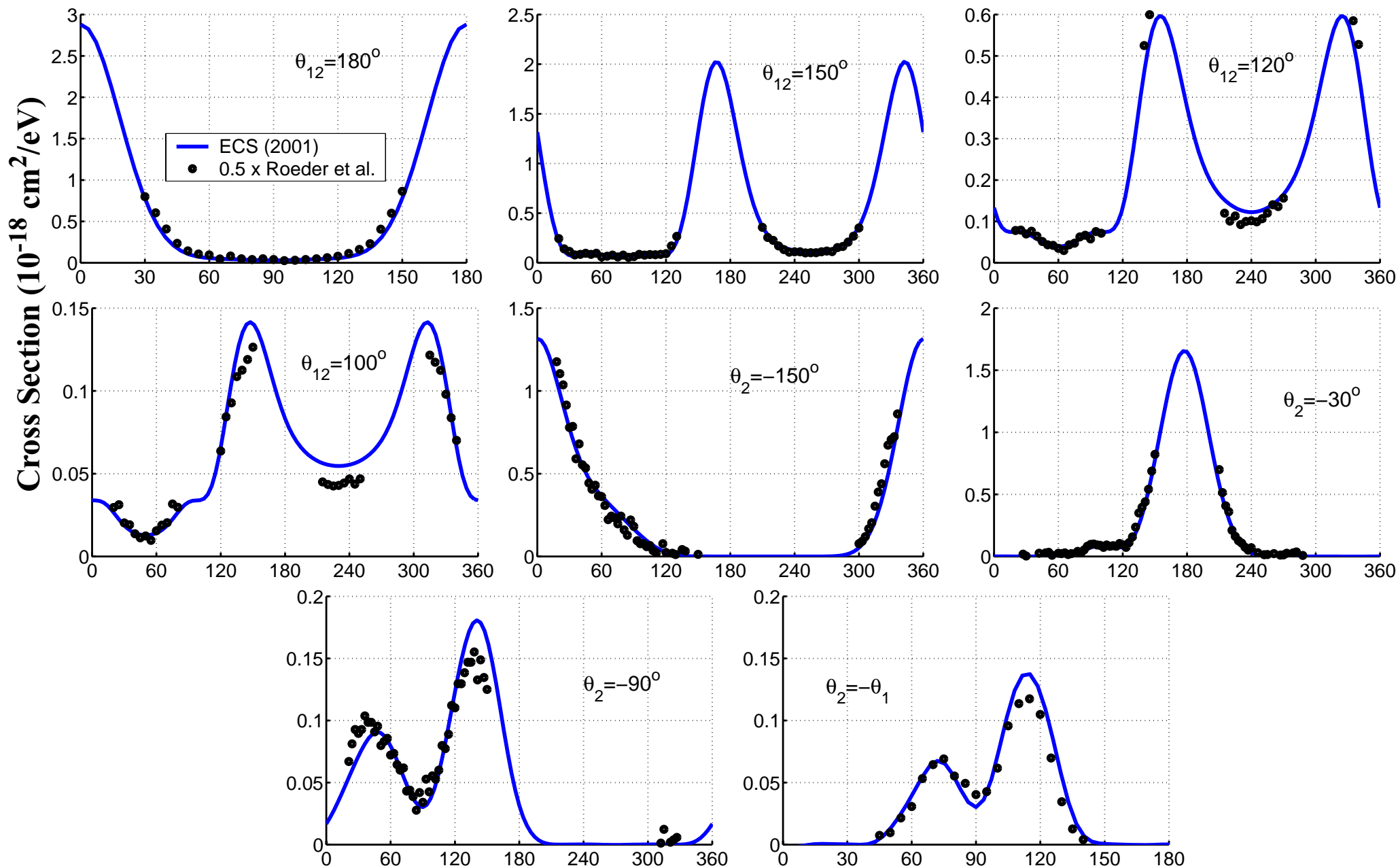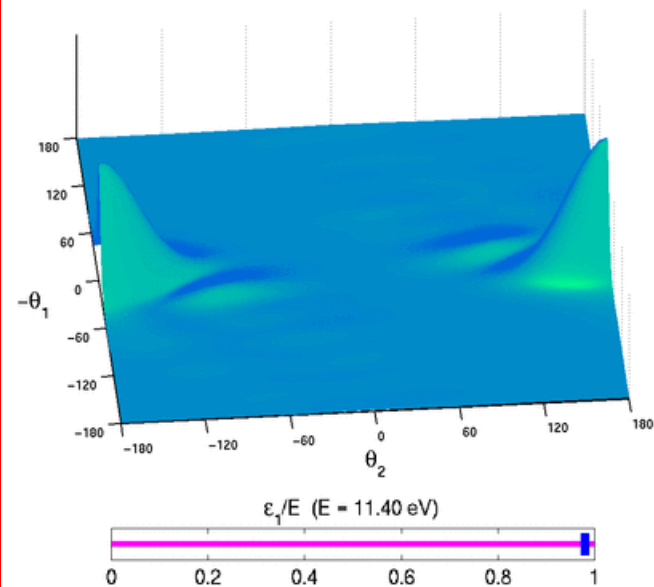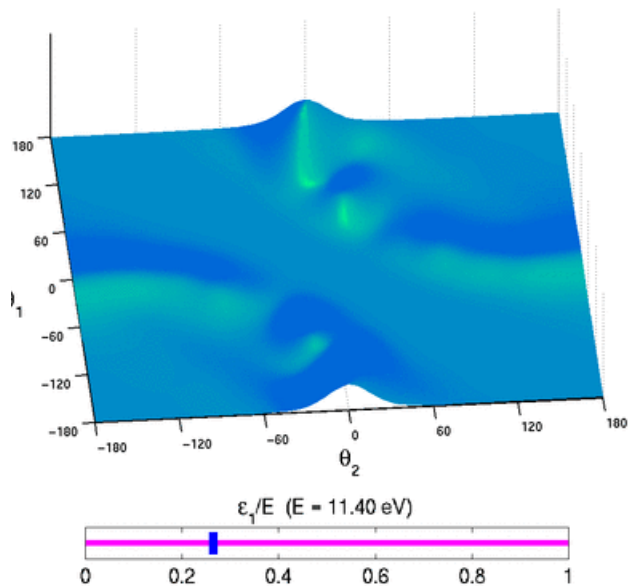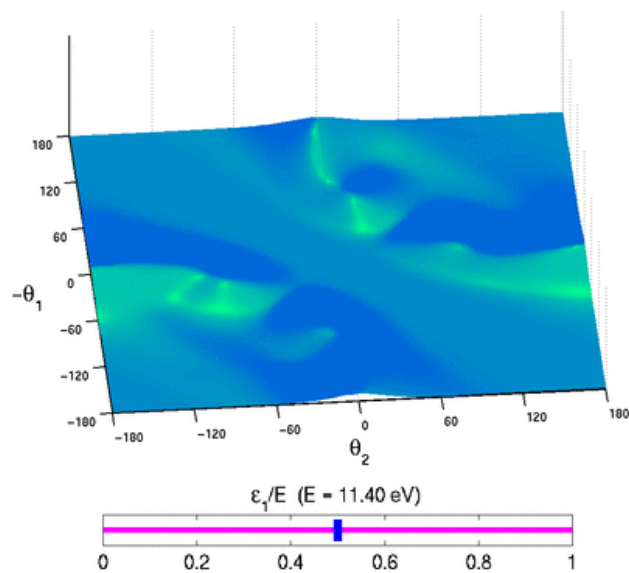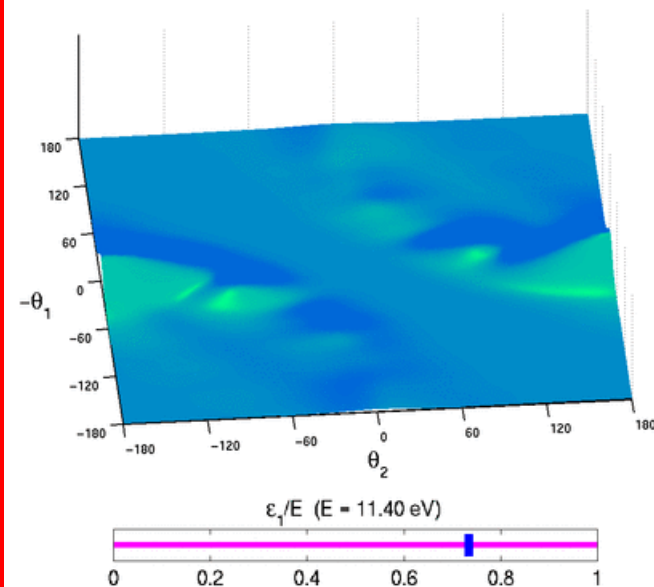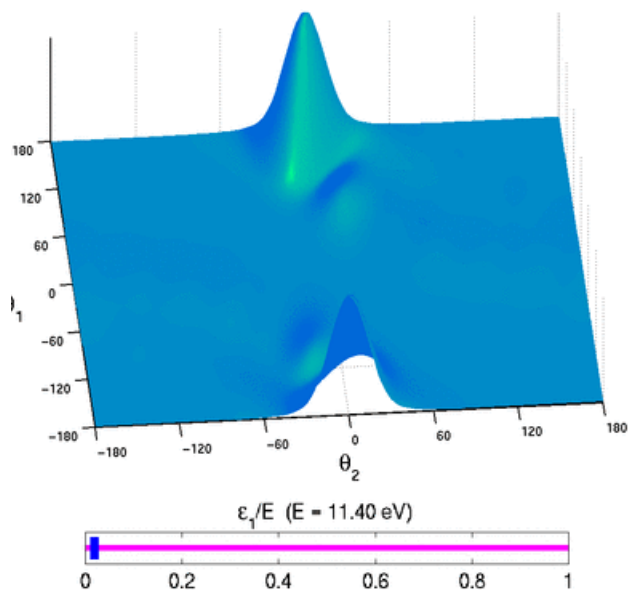
For Electron-Hydrogen Ionization, The Problem Has Been "Reduced To Computation"

Triply Differential Cross Sections -- Symmetric Coplanar 25eV (from integral form)

Unequal **Energy Sharing:**
Triply Differential Cross
Sections at 25 eV --
Recent Results of M.
Baertschy

BUT

A complete solution of the simplest THREE-ELECTRON example is necessary to form the basis for a theory for many-electron atoms and molecules, because three electrons are required for a system to display the basic processes:
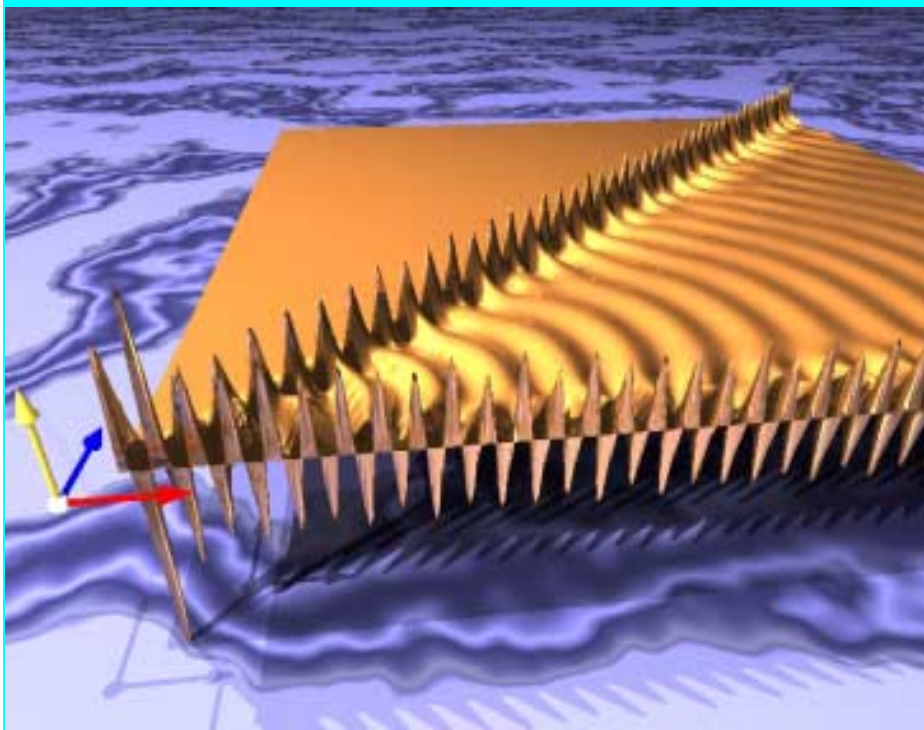
Direct ionization: $e^- + He \rightarrow He^+ + 2e^-$
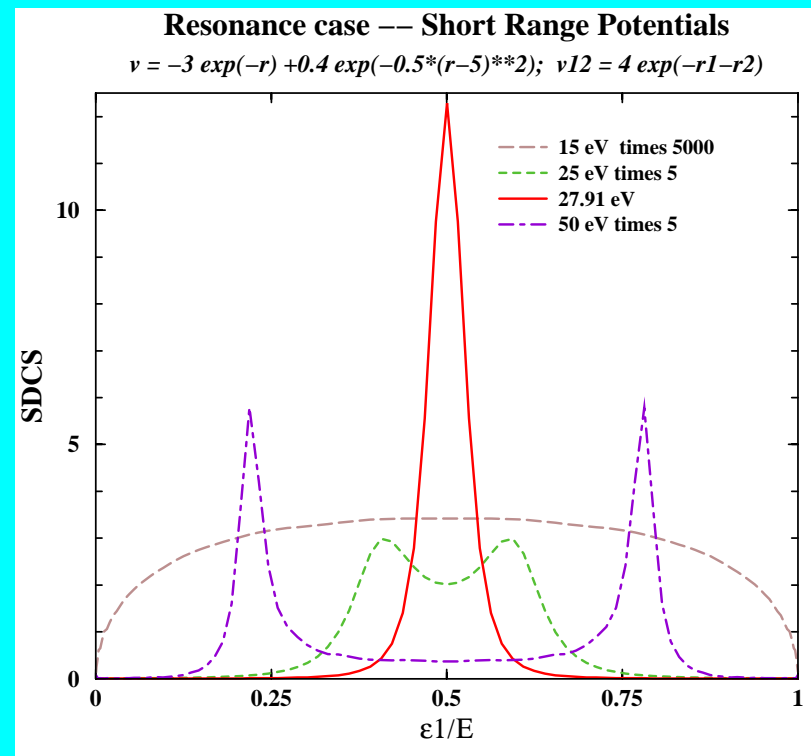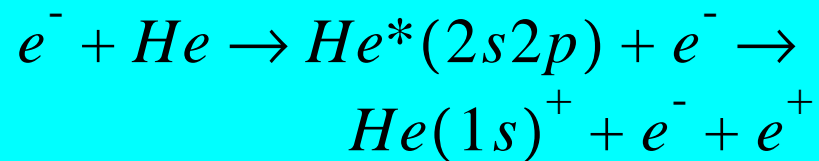
Excitation ionization: $e^- + He \rightarrow (He^+)^* + 2e^-$

Excitation autoionization: $e^- + He \rightarrow He^*(2s2p) + e^- \rightarrow$
$$He(1s)^+ + e^- + e^-$$

Multiple ionization: $e^- + He \rightarrow He^{++} + 3e^-$

Other Physical Phenomena in Collisional Ionization

Multielectron target atoms: Autoionizing states and their interference with direct ionization.

$$e^- + He \rightarrow He^*(2s2p) + e^- \rightarrow$$
$$He(1s)^+ + e^- + e^+$$

Resonance case –– Short Range Potentials

v = −3 exp(−r) +0.4 exp(−0.5*(r−5)**2); v12 = 4 exp(−r1−r2)

Legend:
- 15 eV times 5000
- 25 eV times 5
- 27.91 eV
- 50 eV times 5

Axes: SDCS (vertical), $\varepsilon 1/E$ (horizontal)

Positronium impact ionization: Positronium formation together with ionization -- currently no complete approach to separate them above the ionization threshold.
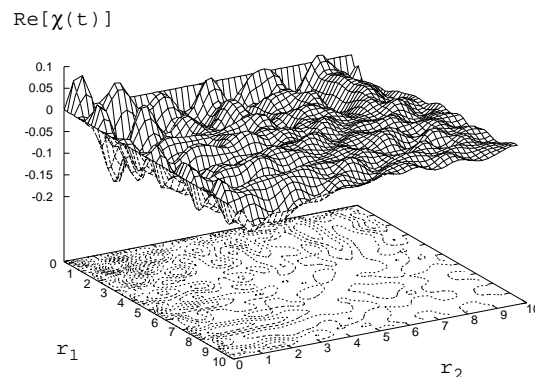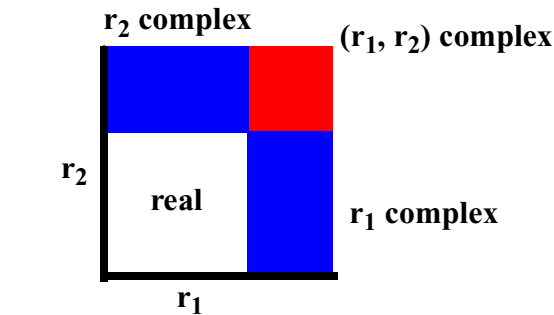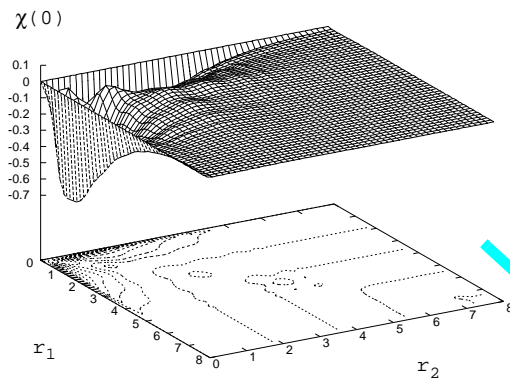
$$e^+ + A \rightarrow A^+ + e^- + e^+$$

$$e^+ + A \rightarrow A^+ + Ps$$
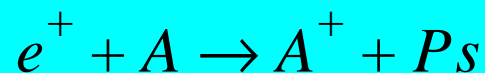
Time-Dependent Approach to Electron Impact Ionization with Exterior Complex Scaling

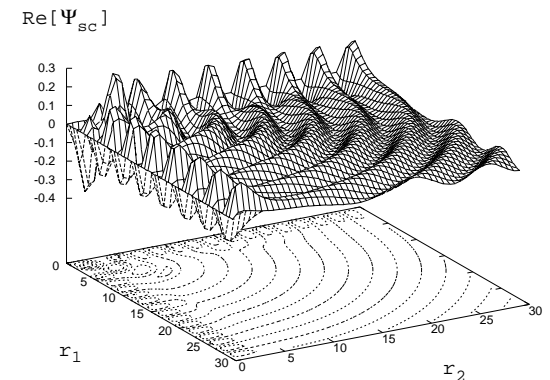**The driven Schrödinger Equation,** $(H - E)|\Psi^+_{sc}\rangle = (H - E)|\Phi^0_{\mathbf{k}_0}\rangle$

can be formally converted to

$$|\Psi^+_{sc}\rangle = \frac{1}{i}\int_0^\infty e^{iEt}e^{-iHt}(H - E)|\Phi^0_{\mathbf{k}_0}\rangle dt = \frac{1}{i}\int_0^\infty e^{iEt}\chi(t)dt$$

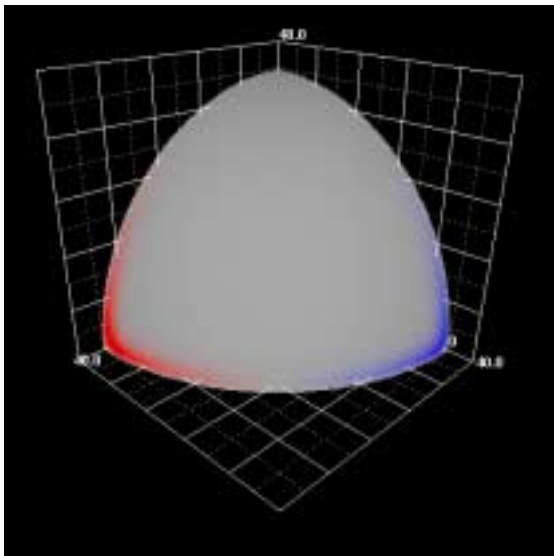**Exterior Complex Scaling *exactly* removes reflections at the boundaries**

$\chi(0)$

r_2 complex

(r_1, r_2) complex

r_2

real

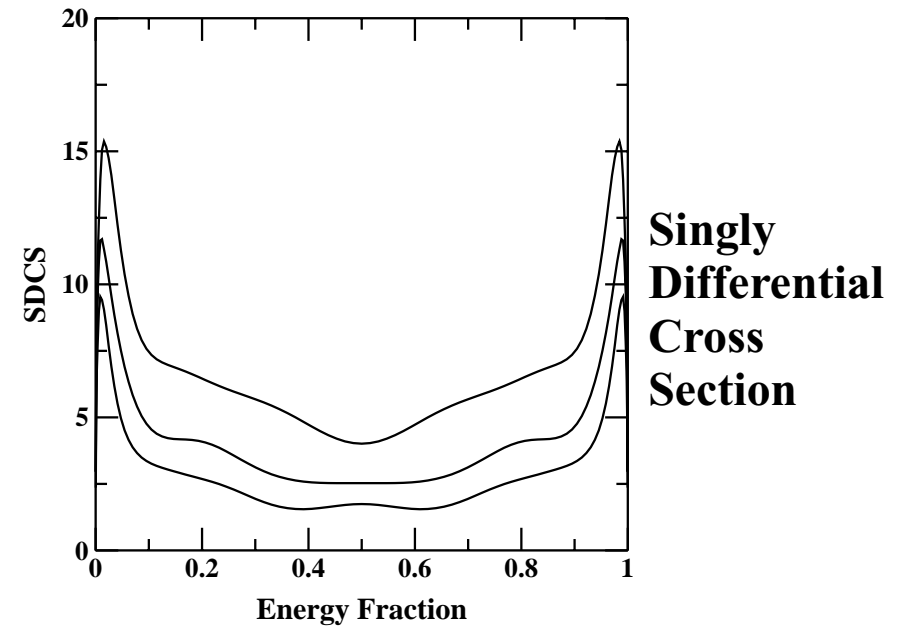r_1 complex

r_1

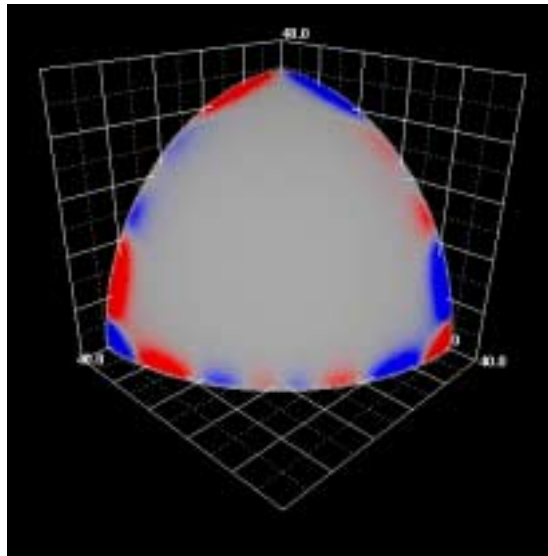**Fourer Transform**

$Re[\Psi_{sc}]$

$Re[\chi(t)]$

First, a proof of principle: A model three-electron breakup problem with short-range potentials

Model Hamiltonian

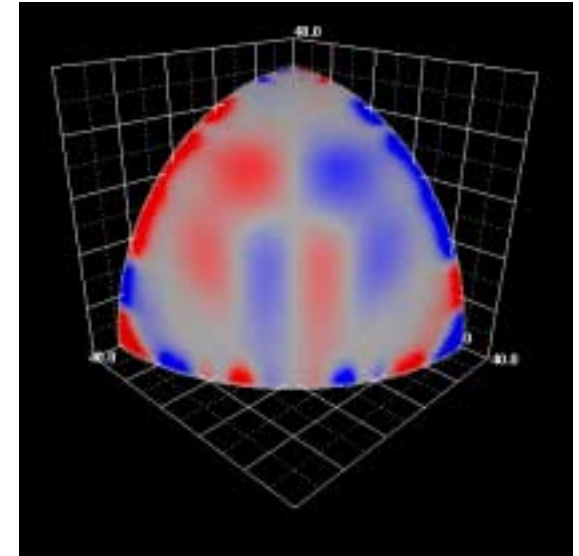$$H = \sum_i (T_i - 3e^{-r_i}) + \sum_{i>j} 9e^{-(r_i + r_j)}$$

Singly Differential Cross Section

E < First I.P

First I.P. < E < Second I.P

E > Second I.P.

Completely Solving the Electron-Impact Ionization for Many-Electron Atoms and Molecules

- The "s-wave" model for electron-Helium: $V = \sum_{i>j} \dfrac{1}{max(r_i, r_j)}$

This model has all of the types of physical processes, including autoionization, that can occur in the three-electron breakup problem.

The current capability, which solves for a single radial function, $\Psi_{sc}^{+}(r_1, r_2, r_3)$, can

be used to completely solve this s-wave model for electron-Helium breakup collisions.

- The full Electron-Helium collision problem, all partial waves coupled, is a supercomputer task, but can use exactly the *same algorithms.*

- This work forms the foundation for an ab initio approach to the electron-impact ionization of molecules at intermediate energies, BUT the details will be different: No grids, but the Exterior Complex Scaling and Time-Propagation will carry over.

Concluding Observations
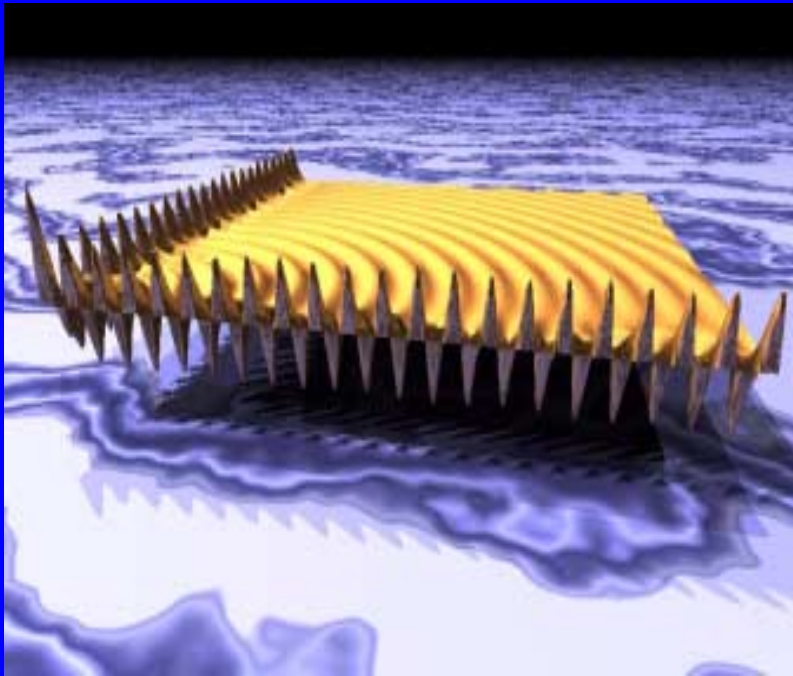
- **The most successful approach to the Coulomb breakup problem avoided the formal boundary conditions (in a rigorous fashion) -- but that may not always be necessary.**

- **A basis for accurate approximations for many electron atoms will require the complete description of ionization of a two-electron target with autoionization + single and double ionization, all treated on the same footing.**

- **In the era of "complexity", some of the highest-end supercomputing was necessary to solve one of the most basic problems in atomic physics .**

Additional Material

The Complex Coordinates Idea

- (Early theorems: Aguilar, Balslev, Combes and Simon -- 1970s)
- (Early computations: Doolen, Nuttall et al -- 1970s.)

Scale the coordinates of all particles according to $\vec{r}_j \to \vec{r}_j e^{i\vartheta}$

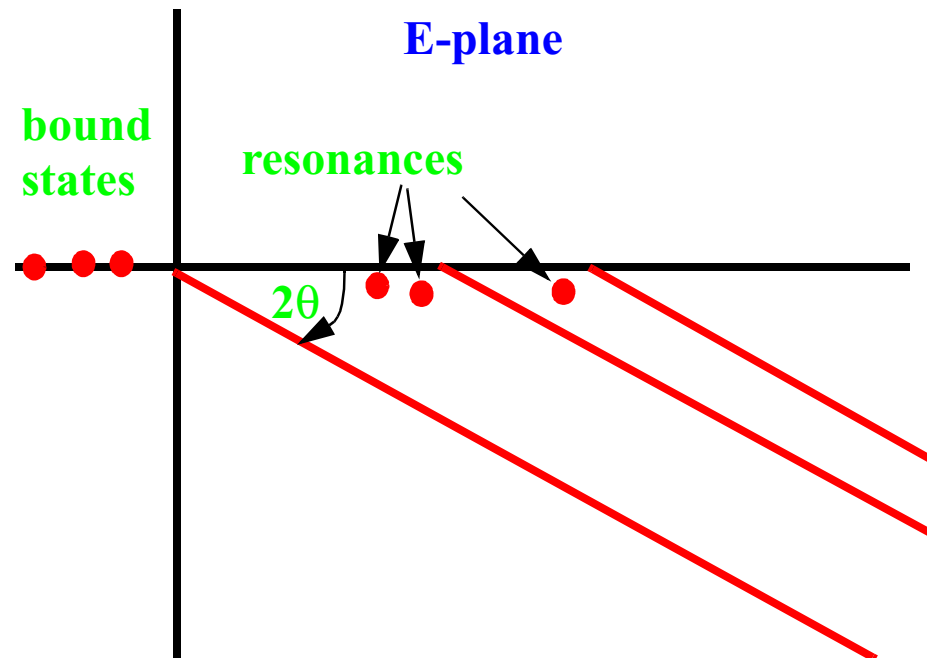**Spectrum of** $H_\vartheta = H(\vec{r}_j e^{i\vartheta})$,

$H_\vartheta \Psi = E_\vartheta \Psi$ **for dilation analytic**

potentials, e.g. Coulomb:

Resonance wave functions at

$E = E_r - i\Gamma/2$ **become square integra-**

ble

$\lim_{r_j \to \infty} \Psi_{res} = 0$ **and hence can be**

E-plane

bound states

resonances

2θ

expanded in a basis. Better yet, for Coulomb interactions: $H = e^{-2i\vartheta} T + e^{-i\vartheta} V$, **so**

no new matrix elements are needed! $T = \sum \frac{1}{2m}\nabla^2$ **and** $V = \sum 1/\left|\vec{r}_i - \vec{r}_j\right|$

Complex Coordinates for a One-Particle System

Continuum:

$$\Psi(r) \underset{r \to \infty}{\longrightarrow} \sin(kr + \delta) \qquad \text{so under scaling } \Psi_\vartheta(r) \underset{r \to \infty}{\longrightarrow} \sin(kre^{i\vartheta} + \delta)$$

$$\text{but } \Psi_\vartheta(r) \underset{r \to \infty}{\longrightarrow} \sin(k_\vartheta re^{i\vartheta} + \delta) \to \text{finite} \qquad \text{requires } k_\vartheta = ke^{-i\vartheta}$$

$$\text{and } E_\vartheta = \frac{k_\vartheta^2}{2m} = \frac{k^2 e^{-2i\vartheta}}{2m} \qquad \text{so the continuous spectrum "rotates"}$$

Resonances:

$$\Psi^{res} \underset{r \to \infty}{\longrightarrow} e^{ik_{res}r} \qquad \text{with } k_{res} = |k_{res}|e^{-i\alpha} \quad \Psi_\vartheta^{res} \underset{r \to \infty}{\longrightarrow} e^{i|k_{res}|e^{-i\alpha}re^{i\vartheta}} \to 0$$

If $\vartheta > \alpha$ **the resonance wave function is square-integrable with** $E_{res} = k_{res}^2/2m$

Real Energy (Hermitian)Discrete Spectral Representation Fails

$$\sum_{n=1}^{N} \langle f|\phi_n\rangle \frac{1}{E - E_n} \langle \phi_n|g\rangle \rightarrow \lim_{\varepsilon \to 0} \langle f|(E - H + i\varepsilon)^{-1}|g\rangle$$
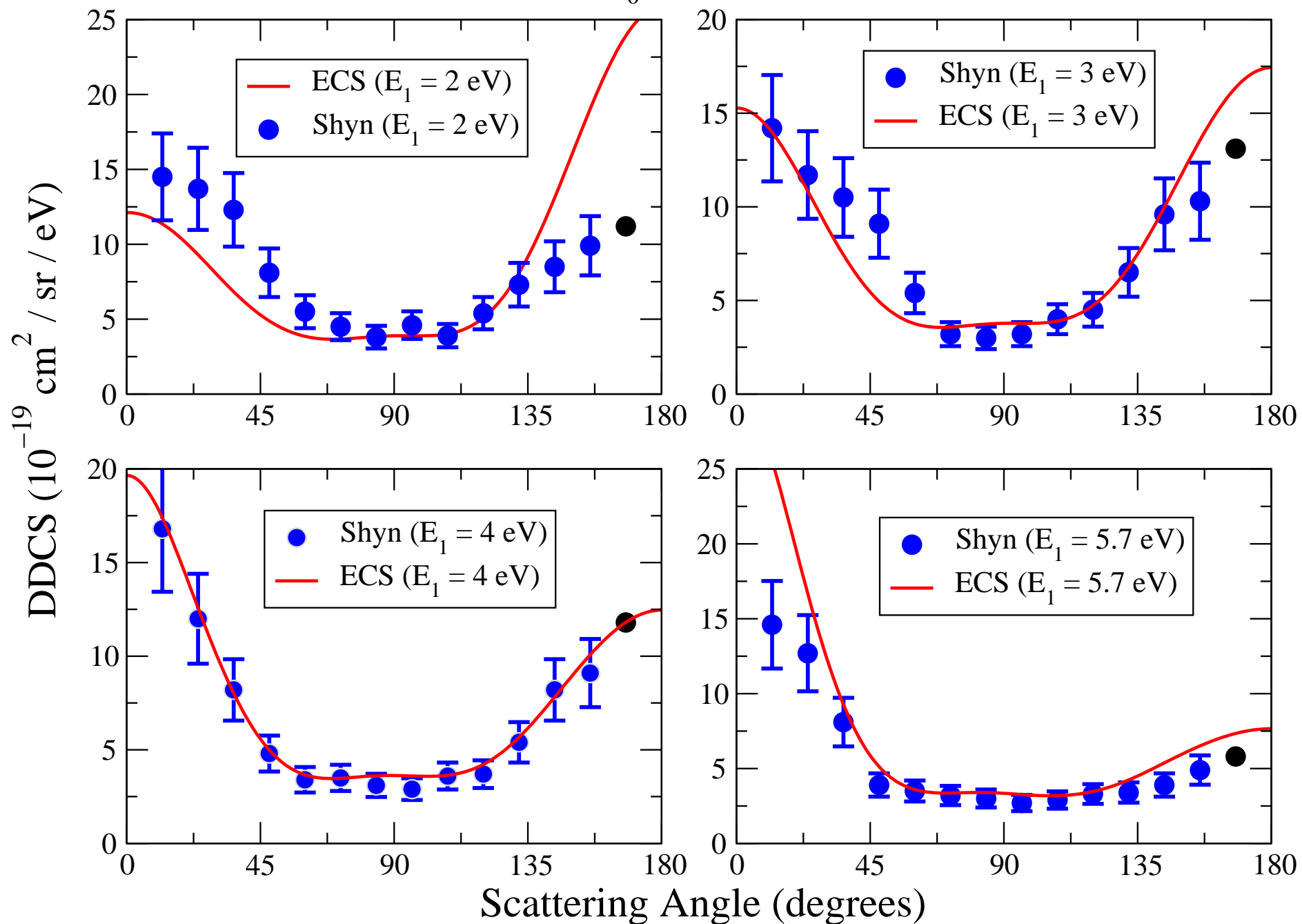
because the singularities at $E = E_n$ **arise from the periodic motion due to reflections in a finite "box" imposed by the finite basis.**

But Complex coordinates (or complex basis function method) fix the discrete spectral representation, because they *eliminate the reflections from the box edges.*
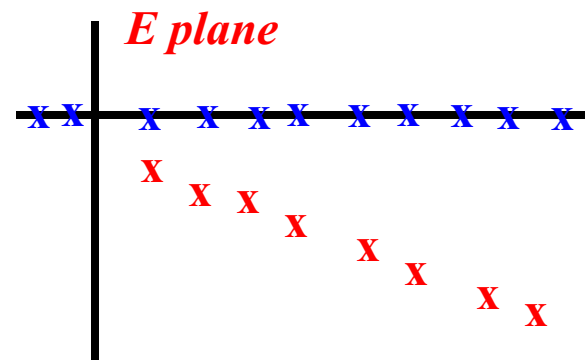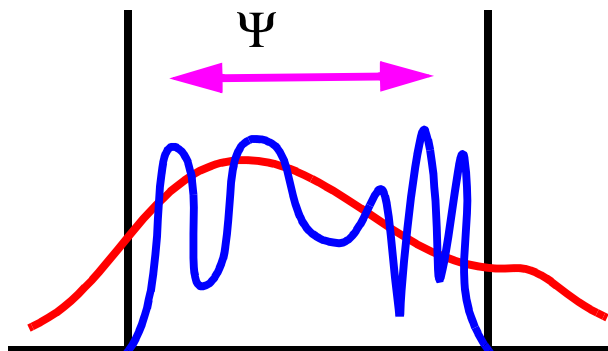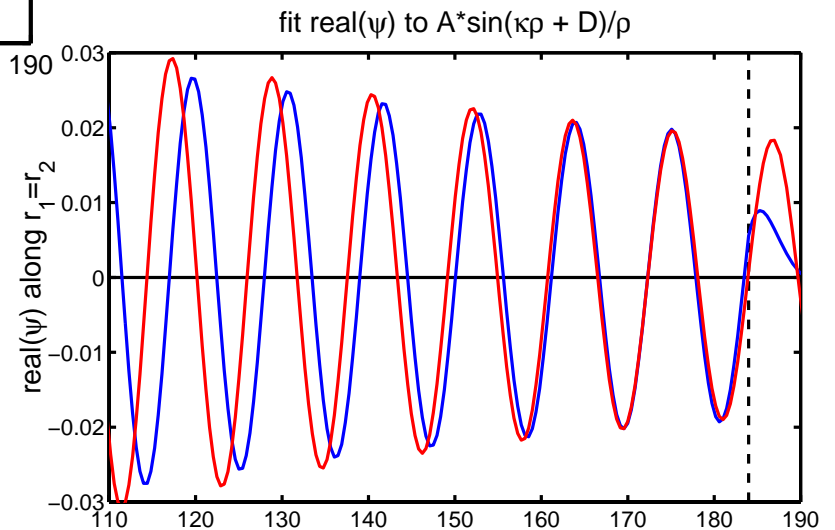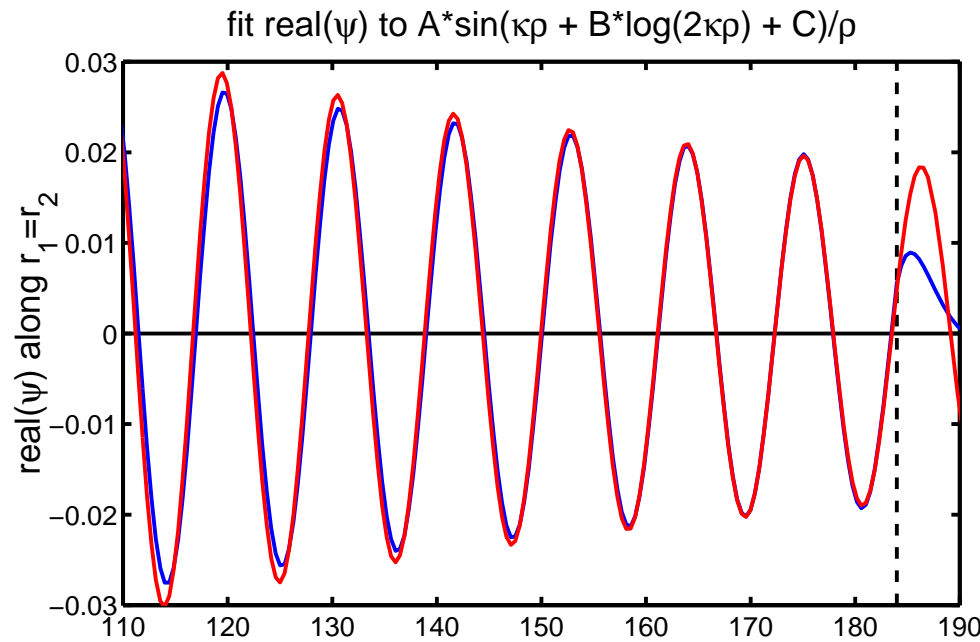
e⁻ – H Doubly Differential Cross Section

Exterior Scaling Retains the Coulomb Logarithmic Phases

fit real(ψ) to A*sin($\kappa\rho$ + B*log($2\kappa\rho$) + C)/ρ

fit real(ψ) to A*sin($\kappa\rho$ + D)/ρ

# Amplitudes in the Formal Theory of Ionization

The natural way to write the amplitude for breakup is

$$F(\vec{k}_1, \vec{k}_2) = \langle \Phi^{(-)}_{\vec{k}_1, z_1} \Phi^{(-)}_{\vec{k}_2, z_2} | V_{12} | \Psi^{(+)} \rangle$$
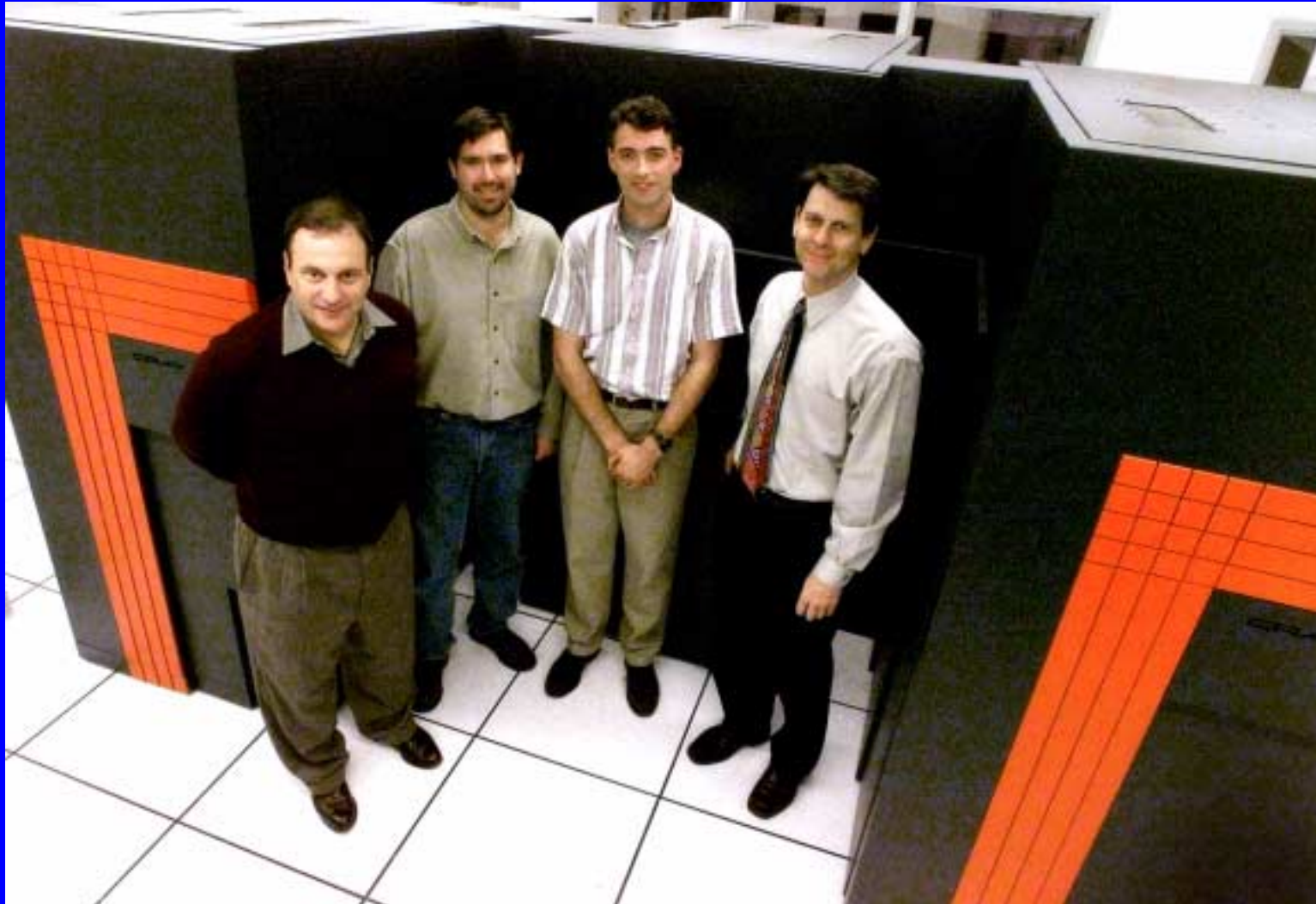
But Rudge and Peterkop pointed out that *for Coulomb potentials* if the integration volume is infinite, this expression has an infinite phase! Unless the charges satisfy the angle and energy dependent condition:

$$\frac{z_1}{k_1} + \frac{z_2}{k_2} = \frac{1}{k_1} + \frac{1}{k_2} - \frac{1}{\left| \vec{k}_1 - \vec{k}_2 \right|}$$

Triple Differential Cross Section 17.6 eV
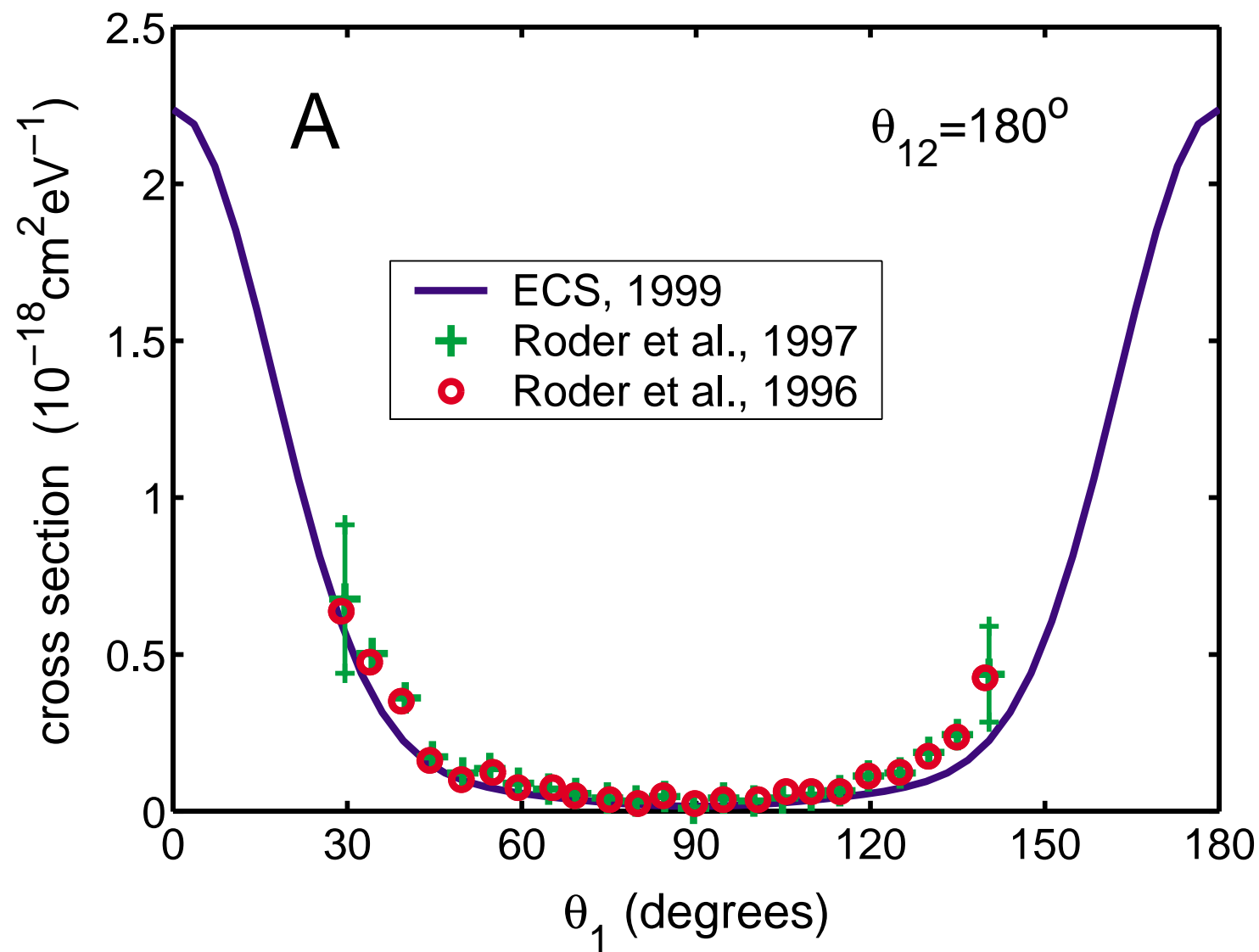
The Experimental Apparatus

Cray T3E

A New Problem in Computing the Breakup Amplitude in the Three-Electron Case

For two-electrons orthogonality of the one-body continuum and bound functions simplifies the calculation, but in the three-electron case no such orthogonality exists. Arrangements can not be made orthogonal.

$$f_{ion} = \langle \varphi_{k_1} \varphi_{k_2} | E - T - V_1 | \Psi^+_{sc} \rangle \qquad \Psi^+_{sc} \sim \sum \frac{f_n}{k_n} e^{ik_n r_1} \varphi_n(r_2) + f_{ion} \frac{e^{iK\rho}}{\sqrt{\rho}}$$

$$f^m_{ion} = \langle \varphi_{k_1} \varphi_{k_2} \varphi_m | E - T - V_1 | \Psi^+_{sc} \rangle \qquad \Psi^+_{sc} \sim \sum \frac{f_n}{k_n} e^{ik_n r_1} \chi_n(r_2, r_3) + \sum f^m_{ion} \frac{e^{iK\rho_{12}}}{\sqrt{\rho_{12}}} \varphi_m(r_3)$$

$$\langle \varphi_k | \varphi_n \rangle = 0 \text{ BUT } \langle \varphi_k \varphi_m | \chi_n \rangle \neq 0 \text{ so free-free}$$

overlaps on finite volume survive, and do not

become delta functions.

Solution: "Asymptotic Projection",

$$\Psi^{proj}_{sc} = \Psi^+_{sc} - \sum (f_n / k_n) e^{ik_n r_1} \chi_n(r_2, r_3)$$